AMERICAN
DYESTUFF REPORTER
VOLUME 34 OCTOBER 8, 1945 NUMBER 21

Some Chemical Aspects of WOOL PROTEIN BEHAVIOR

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PROTEINS AND AMINO ACIDS

THERE occurs in nature a group of allied products of life which man calls proteins. A rough but serviceable division of these compounds into related classes is made on the basis of differences in properties,* and a brief list is useful for the purpose of orientation. Examples are: the *albumin* of egg white, milk, and blood (lactalbumin in milk); the *globulin* of seeds and blood (edestin in hempseed); the *glutelin* of seeds (glutenin in wheat); the *prolamin* of cereal grains (zein in maize); the *albuminoids* of animal tissues (elastin in ligaments and arterial walls, collagen in connective tissue, keratin in hair); the *histone* of animal glands; and the *protamin* of fish sperm.

The chemical structure of the simplest of the proteins, if any is notably simpler than others, is not known, but certain empirical data have made plausible guessing possible. Probably the most significant single fact is that treatment with strong acids, strong bases, or proteolytic enzymes results in hydrolytic splitting of the protein molecule, yielding what seem to be the building blocks of this complex structure, α amino acids.

Twenty-two amino acids have been isolated from simple** protein hydrolysates, while over a dozen others have been reported but not verified.† These amino acids are most conveniently divided into neutral, acid, and basic classes: glycine, $NH_2CH_2.COOH$, the simplest naturally occurring amino acid, has one acid (—COOH) group and one basic ($—NH_2$) group; aspartic acid, $HOOC.CH_2CH.NH_2COOH$, has one acid group in excess; while lysine, $NH_2(CH_2)_4.NH_2.COOH$, has one basic group in excess.

The problem of the chemical structure of protein resolves itself initially into a search for the most logical way in which the amino acids can be linked together to form the very much larger protein unit.

In a series of experiments which have since become widely known and quoted, Fischer[1] succeeded in reversing the process of hydrolysis when he coupled some of the amino acids to produce what he called polypeptides. From the evidence at hand he thought it highly probable that his peptide linkage was through the acid (carboxyl) group of one amino acid to the basic (amino) group of another, accompanied by a loss of water:

$$NH_2.R.COOH + NH_2.R'.COOH \rightarrow NH_2.R.CO.NH.R'.COOH + H_2O‡$$
a di-peptide

Repeated coupling gave a polypeptide with a molecular weight of 1213. Had it been found in nature it would probably have been classed as a protein; however, since the molecular weight of a relatively small molecule like that of egg albumin may be about 34,000, the suggested analogy should be drawn with caution.

Hofmeister,[2] a contemporary of Fischer, reviewed the available evidence, and eliminating several possible amino acid linkages, accepted the peptide linkage as the one solution which most adequately fitted the data.

Other theories have been proposed to describe the linkages of amino acids in proteins,[3] but, quoting Block,[4] "the peptide hypothesis has been the only theory on the structure of the protein molecule which has thoroughly withstood the test of time and experimentation, and upon it are based the only protein theories which have o tained acceptance during the past 25 years."

ADDITIONAL LINKAGES IN WOOL PROTEIN

For a fibrous protein like wool, whose uni-directional orientation (cortical) can be observed down to the range of the electron microscope[5] the polypeptide hypothesis seems particularly fitting; but it seems likely that it does not tell the whole story. There can be little doubt after considering the convincing evidence which had been presented, that the peptide chains in wool are cross-linked by the amino-acid cystine.[6,7] This linkage is illustrated in Fig. A.

Several reasons (the principal one will be discussed later) led Speakman[8] to believe that salt (ester) cross-linkages also exist in wool. The participating groups are the extra amino (imino) and carboxyl groups of the diacid and dibasic amino acid residues. The linkage is most conveniently illustrated with glutamic acid and lysine side chains. (See Fig. B.)

ACID AMIDES

The fact that wool and other proteins are not so strongly acid as the large amounts of aspartic acid and glutamic acids they contain would indicate is attributed to the presence of acid amides. Two more reasons for this conclusion are: More or less definite amounts of ammonia can be released from a protein under conditions too mild to cause the disruption of primary amines or the peptide linkage; and, the primary amides, asparagine and glutamine, have been isolated from proteins.[9] The aspartic acid

* Such as relative solubility in water, acid, basic, or salt solutions; solubility in organic solvents; resistance to enzyme digestion; coagulability; and proportional presence, or absence of specific constituents.

** Distinct from complex proteins, which yield non-protein material as well as amino acids upon hydrolysis.

† 'Verification' consists in meeting specified requirements. These are listed by M. Dunn, in C. Schmidt, Chem. of Amino Acids & Proteins, Charles C. Thomas Co., Springfield, Ill., (1944) pp. 21-22; the same chapter contains a list of unverified amino acids, with a discussion of each. Possibility of the existence of as many as 52 amino acids is discussed by Dunn in the Addendum of the same book (p. 1035).

‡ Schematic only; in actually synthesizing the first di-peptide, Fischer used the ethyl ester of glycine, which in water forms glycine anhydride, split this ring with hydrochloric acid, and obtained glycyl-glycine:

$$2\ NH_2.CH_2.COC_2H_5 \xrightarrow{H_2O} \begin{matrix} NH.CH_2.CO \\ | \quad\quad | \\ CO.CH_2.NH \end{matrix} \xrightarrow{HCl} NH_2.CH_2.CONH.CH_2COOH$$

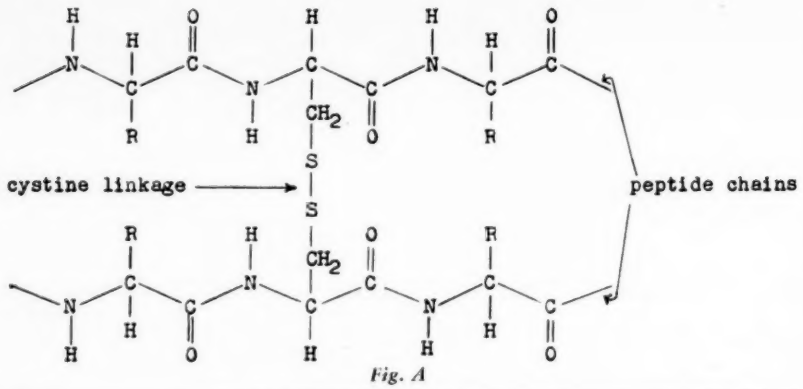


Fig. A

residue, combined in acid amide form (asparagine), is shown in Fig. C.

WOOL HYDROLYSIS

Wool is an albuminoid protein, keratin, insoluble in water, dilute acid, alkaline or salt solutions, insoluble in organic solvents, and resistant to digestion by proteolytic enzymes. It may be hydrolyzed into its constituent amino acids with the help of strongly acid or alkaline solutions. Neither sulfuric acid nor sodium hydroxide yields a clear hydrolysate. A quietly refluxed 35 per cent solution of sulfuric acid (1/70 bath) dissolves wool in about 20 minutes, giving a slightly turbid, light brown solution, which becomes darker and possibly more turbid on prolonged boiling (24 hours); a gently refluxed 5 per cent sodium hydroxide solution (1/70 bath) dissolves wool in 2-4 minutes, giving a turbid yellow solution which changes little on prolonged boiling (24 hours). The insoluble matter in both solutions is probably a product of the hydrolysis, rather than a resistant protein residue.

Hydrolytic splitting may occur this way.

(1) $NH_2R.CONH.R'COOH + 2H_2SO_4 + H_2O \rightarrow SO_4H.NH_3R.COOH + SO_4H.NH_3R'COOH$

(2) $NH_2R.CONH.R'COOH + 2NaOH + H_2O \rightarrow HONH_2R.COONa + HONH_2R'COONa$

COMPOSITION OF THE WOOL HYDROLYSATE

Quantitative determination of amino acids in the keratin hydrolysate is difficult. Results in many cases do not even approximate 100 per cent recovery.* Wool, almost without doubt, is composed of more than one type of keratin,[9] and proportions of the different types may not be constant. Geiger[10] has shown that the relative amounts of some amino acids in cortical and scale cells differ.** The sulfur content varies over the length of a single fiber.[11] These and other considerations indicate that analysis figures for proteins cannot be thought of as strictly quantitative; nevertheless they should be regarded as far better than rough approximations.

MINIMUM MOLECULAR WEIGHT OF WOOL

Harris, Mizell and Fourt[12] have compiled a table of the amino acid content of wool hydrolysates, from sources listed in their bibliography. From these figures can be computed the approximate minimum molecular weight of wool keratin (Table 1).

Hydroxlysine, the component appearing in the lowest percentage, is reported to two significant figures, and its value is logically the unit to use in computing this weight; but to make its position more secure, the possibly more reliable value for methionine (also reported to two significant figures) was assigned an even 4, changing the hydroxlysine factor from .0013 to .0012. This choice of factor was not the only possible choice, but it seemed the best substantiated, since the two other low analysis values were reported to but one significant figure.

It must be stressed that these calculations can lead only to a tentative first guess: too many uncertainties enter in to justify more than provisional acceptance of the value 84,500, as being roughly of the right order of magnitude for the molecular weight of wool.

POTENTIALLY REACTIVE ('FREE') GROUPS IN WOOL

If we accept the Fischer peptide-chain hypothesis of protein structure, and the concept of cystine cross-linkage in wool keratin, every molecule of amino acid participating in the wool molecule structure other than cystine will have one amino and one carboxyl group bound in peptide linkage; an inspection of wool hydrolysis products will show that the remaining polar groups must come from dibasic and diacid amino acid residues. An exception must occur if discreet molecular units appear as such in keratin†: the ends of the chain‡ would have

* 100% recovery would mean 110-120% actually, because each amino acid residue takes on 1 molecule of water upon hydrolysis.

** This may not be of practical significance in an analysis, since Geiger states that scale cells may represent only 2.5% of the weight of wool fiber.

† This seems unlikely but finds support in Dunn's[14] statement that free amino nitrogen 'considerably in excess of one-half of the lysine nitrogen' can be liberated from the protamin of "Sardinia caerulea" by nitrous acid.

‡ More than one chain can be visualized in a cross-linked protein molecule. In wool the number of known or suspected 'free' groups from other sources seems to account fully for known reactivity, and therefore favors a minimum of reactive peptide-chain end groups.

Fig. B

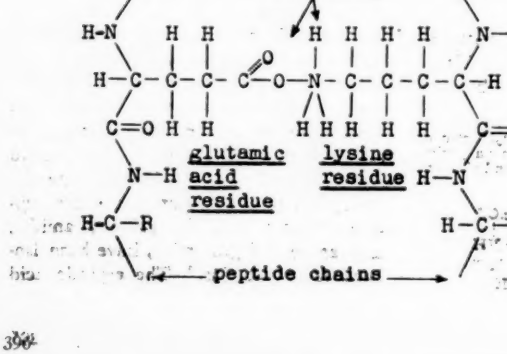


Fig. C

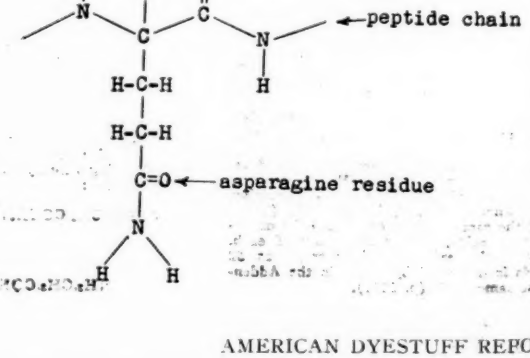


Table 1. Calculation of the Minimum Molecular Weight of Wool

Amino Acid	% by Wt. (A)	Mol. Wt. (B)	Mol. Wt. Residue (B-H₂O)	% by Wt. Residues A(B-H₂O)/B	Numerical Ratio (A/B)	Relative (integral) frequency (C.)	Total Weight [(B-H₂O)xC)]
Glycine	6.5	75	57	4.93	.0865	72	4100
Alanine	4.4	89	71	3.51	.0494	41	2910
Valine	4.72	117	99	3.99	.04031	34	3360
Threonine*	6.76	119	101	5.74	.05681	47	4750
Luecine isomers	11.3	131	113	9.75	.08619	72	8140
Phenylalaine	3.75	165	147	3.34	.02272	19	2790
Tyrosine	5.8	181	163	5.22	.0320	27	4400
Serine	9.41	105	87	7.80	.08962	75	6520
Proline	6.75	115	97	5.69	.05869	49	4750
Tryptophane	0.7	204	186	0.64	.0034	3	560
Methionine	0.71	149	131	0.62	.00476	4	520
Cystine	12.72	240	204	10.81	.053000	44	9770
Aspartic Acid	7.27	133	115	6.29	.05466	45	5170
Glutamic Acid	15.27	147	129	13.40	.10388	87	11200
Lysine	3.3	146	128	2.89	.0226	19	2450
Hydroxylysine*	0.21	162	144	0.19	.00130	1	140
Arginine	10.4	174	156	9.32	.05977	50	7800
Histidine	0.7	155	137	0.62	.0045	4	550
	110.67			94.74		1 H_2O	20
							79,900
Ammonia N	1.18	14			.08425	70	

79,900 — 70 (= —OH to —NH_2) = 79,800.
94.7% = 79,800.
100% = 84,500 = minimum molecular weight of wool.

* Not yet officially recognized as accepted amino acids, though the requirements seem to have been fulfilled in the case of threonine.

a "free" amine, and a "free" carboxyl group. Potentially reactive groups in wool protein are: the extra acid groups of the di-carboxylic amino acids, glutamic and aspartic; the phenolic group of tyrosine; the imino group of the peptide linkage; the indole group of tryptophane; the amino group of lysine and hydroxlysine; the guanidino group of arginine; the imidazol group of histidine; and possibly the amide nitrogen of asparagine and glutamine residues.

Results of experiments have shown that in aqueous solution the number of reactive groups is considerably less than the possibilities indicated above. Schmidt and Czarnetzky[13] found that two equivalents of HCl gas combine with tryptophane, arginine and lysine, while three equivalents combine with histidine. They state that there is no evidence that histidine forms a trichloride in aqueous solution. The amide nitrogen of glycine anhydride, of asparagine, and of the simple peptides tested did not react with HCl gas except in the case of the alanyl-proline linkage (—C(=O)—N=). According to Schmidt, Greenstein found no reaction with this linkage in aqueous solution. Schmidt also thinks tryptophane does not react as a diacid base in aqueous solution, but Eagle and Vickers[15] state that the indole group reacts with diazotized sulfanilic acid.

Harris and Kanagy[16] report the behavior of the guanidino group in arginine hydrochloride and wool (in which this free basic group predominates) toward nitrous acid to be analagous. Schmidt Kirk, and Appleman[17] have found that arginine monohydrochloride combines with 1 equivalent of hydrochloric acid.

The calculations of the combining equivalents of proteins by Schmidt and Czarnetszky are based on the following equivalents:

	Combining values expected in aqueous solution		Combining values expected in gas titrations
Lysine	1		1
Arginine	1		1
Histidine	1		2
Glutamic acid	1	less amounts combined as acid amides.	1
Hydroxy glutamic acid	1		1
Aspartic acid	1		1
Tyrosine	1		1
Tryptophane	—		1
Proline	—		1
Oxyproline	—		1

Goodall and Hobday[18] have presented experimental evidence that the maximum combining power of wool is greater in solutions at boiling temperature than in those at normal temperature (25° C.). However, it would seem that gas titration maxima should mark the upper limit of combining power under all conditions short of destruction of the wool fiber.

The amino acids which contain groups considered to be free in wool are illustrated in Fig. D. The groups are enclosed.

On the basis of the foregoing data, the maximum combining capacity of wool as an acid and a base has been calculated (see Table 2).*

All mention of additional charges on the wool fiber arising from sources other than the dissociation of polar groups has been avoided; even though the possibility of their presence is sufficiently strong to warrant acknowledgement, the problem requires much further research.

DISSOCIATION OF ACIDS AND BASES AS A FUNCTION OF HYDROGEN ION CONCENTRATION

The data in Table 2 show the maximum combining power of wool when the dissociation of the participating groups is complete. It is of at least equal interest to trace these values over the whole dissociation range. The extent of dissociation of the acid and basic groups at any given hydrogen ion concentration, $[H^+]$,** may be calculated from the law of chemical equilibrium.[21]

* Compare with Steinhardt and Harris.[19] In their calculations. tyrosine was included only tentatively. Gleysteen and Harris[20] later obtained evidence that tyrosine is reactive in silk fibroin.
** Brackets refer to concentration of enclosed ion in gram-ions per liter.

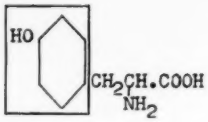
Table 2. Calculation of the Maximum Combining Capacity of Wool

Amino Acid	Percent Residue Found in Wool	Combining Equivalents	Molecular Weight	Combining Wt. Milli-equiv. per Gram of Wool	Total without Amide N	Total with Amide N
Tyrosine	5.2	1	163	.32		
Aspartic Acid	6.29	1	115	.547-.257*		
Glutamic Acid	13.40	1	129	1.039-.489*	1.91	
Amide Nitrogen	1.18	1	14	.84		1.07
Lysine	2.9	1	128	.226		
Hydroxylysine	.19	1	144	.013		
Arginine	9.3	1	156	.598		
Histidine	0.6	1	137	.045	0.88	0.88

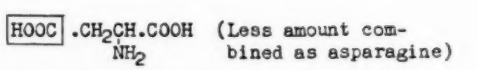
* The first figure is calculated as if acid amides were present, the second as if they were absent. The amide nitrogen was distributed proportionally between aspartic and glutamic acids.

Acid amino acids

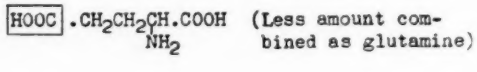
1) Tyrosine - phenolic group



2) Aspartic acid - β carboxyl group

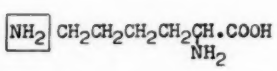


3) Glutamic acid - γ carboxyl group

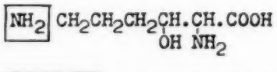


Basic amino acids

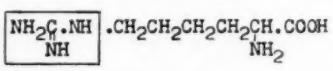
1) Lysine - ε amino group



2) Hydroxylysine - ε amino group



3) Arginine - guanidino group



4) Histidine - imidazol group

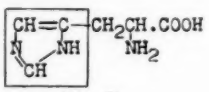


Fig. D

In the case of a solution of an acid, HA, a state of equilibrium is reached when the speed of its dissociation into hydrogen ions and acid anions eventually slows down until it equals the speed of re-association of the ions,

$$HA \rightleftharpoons H^+ + A^-$$

Under given conditions, from the law of chemical equilibrium,

$$\frac{[H^+]\ [A^-]}{[HA]} = \text{an acid dissociation constant, } k_a^*$$

In the above expression,

$$[H^+] = [A^-]$$

Therefore,

$$\frac{[H^+]^2}{k_a} = [HA]$$

The degree of dissociation of the acid, α, is equal to the hydrogen ion concentration divided by the concentration of the total acid, or,

$$\alpha = \frac{[H^+]}{[\text{Total Acid}]}$$

Substituting,

$$\alpha = \frac{[H^+]}{\frac{[H^+]^2}{k_a} + [H^+]}$$

Or,

$$\alpha = \frac{k_a}{[H^+] + k_a} \qquad (1.$$

Similarly, in the case of a base, BOH,

$$BOH \rightleftharpoons B^+ + OH^-$$

$$\frac{[B^+]\ [OH^-]}{[BOH]} = k_b$$

$$\alpha = \frac{k_b}{[OH^-] + k_b} \qquad (2.$$

The values for the dissociation constants, k, are numerically equal to the $[H^+]$ or $[OH^-]$ at which dissociation of an acid or base equals 50 per cent, since when $[H^+]$ or $[OH^-] = k$, it follows from (1) or (2) that $\alpha = \frac{k}{k+k} = \frac{k}{2k} = \frac{1}{2}$.

When the value of a dissociation constant is used in the sense of the midpoint of the dissociation curve, it is called the dissociation index, and is usually designated as the pK value.

The values in table 3 have been calculated from equation (1) for the case in which the dissociation index $= 1 \times 10^{-7}$.

Figure 1 illustrates the curve obtained from the above data.

DISSOCIATION OF AMINO ACIDS

The classical dissociation constants of amino acids represent the amino and carboxyl groups to be remarkably weak, in contrast to expectations based upon the dissociation of compounds containing similar groups, such as ammonium hydroxide and acetic acid. This difficulty, and associated difficulties were resolved in 1923 by Bjerrum[23], who presented evidence in support of the concept of 'zwitterion' dissociation of amino acids, an interpretation which gives the constants more reasonable values.

In 1923, as the result of an attempt to generalize and clarify the whole idea of acids and bases, Bronsted[24] proposed a significant modification in the scheme of acid and basic dissociation in which all constants are acid constants,** directly expressed in terms of a single scale, $[H^+]$ or pH.

The chemical equilibria involved in these three ideas of dissociation and the interrelations of the constants are shown below, and tabulated in table 4.

CLASSICAL FORMULATION OF THE DISSOCIATION OF AMINO ACIDS

In the equations which follow, the formulas for amino acids have been generalized by letting R stand for any alkyl or alkyl-aryl nucleus. The acid dissociation equations were written without including water, but the expressions for basic dissociation required the use of water. Hitchcock[33] illustrates basic dissociation from a hydrated molecule, explaining that "... no distinction is made between the hydrated and unhydrated forms of the uncharged molecule, since the amount of each is a constant fraction of their sum, which is all that has been determined by experiment."

(Continued on Page 407)

* More strictly, $\frac{a_{H^+}\ a_{A^-}}{a_{HA}} = k$, a being the 'activity' of an ion as defined by G. N. Lewis[25]. In very dilute solutions the classical expression remains valid, but as they become more concentrated, activity and concentration diverge.

** Bronsted demonstrated that acids can be considered to be H^+ suppliers, and bases H^+ acceptors.

Table 3. Dissociation of an Acid whose Dissociation Index $= 1 \times 10^{-7}$ as a Function of pH

$[H^+]$	pH*	% Dissoc.	$[H^+]$	pH	% Dissoc.	$[H^+]$	pH	% Dissoc.
$>2.0 \times 10^{-5}$	<4.7	0+	5.0×10^{-7}	6.3	17	1.0×10^{-8}	8.0	91
2.0	4.7	0.5	4.0	6.4	20	7.9×10^{-9}	8.1	93
1.6	4.8	0.6	3.2	6.5	24	6.3	8.2	94
1.3	4.9	0.8	2.5	6.6	28	5.0	8.3	95
1.0	5.0	1.0	2.0	6.7	33	4.0	8.4	96
7.9×10^{-6}	5.1	1.2	1.6	6.8	39	3.2	8.5	97
6.3	5.2	1.6	1.3	6.9	44	2.5	8.6	97.5
5.0	5.3	2.0	1.0	7.0	50	2.0	8.7	98.1
4.0	5.4	2.5	7.9×10^{-8}	7.1	56	1.6	8.8	98.4
3.2	5.5	3	6.3	7.2	61	1.3	8.9	98.8
2.5	5.6	4	5.0	7.3	67	1.0	9.0	99.0
2.0	5.7	5	4.0	7.4	72	7.9×10^{-10}	9.1	99.2
1.6	5.8	6	3.2	7.5	76	6.3	9.2	99.4
1.3	5.9	7	2.5	7.6	80	5.0	9.3	99.5
1.0	6.0	9	2.0	7.7	83	<5.0	>9.3	100-
7.9×10^{-7}	6.1	11	1.6	7.8	86			
6.3	6.2	14	1.3	7.9	89			

* pH = — log $[H^+]$.

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American Association of Textile Chemists and Colorists

OCTOBER 8, 1945

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STUDENT CHAPTERS

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Evaluation of FABRIC PEST DETERRENTS

Tentative Method

WOOL

SCOPE

1. This method of test covers the biological procedure for determining the resistance to insect pests of fabrics or yarns which contain wool or other susceptible fibers. The term, "insect pest," shall be construed to apply to webbing clothes moths and black carpet beetles larvae.

TEST SPECIMENS

2. (a) *Fabrics*—At least 4 specimens, with an area of one or two square inches shall be cut from widely spaced portions of the fabric to be tested.

(b) *Yarns*—At least 4 specimens shall be prepared by winding the yarn on a piece of glass or metal 1½" x 1½". The surface of the metal or glass shall be substantially covered by the yarn.

(c) *Control Specimens for Larvae Activity*—At least 4 standard specimens of pure undyed scoured wool fabric shall be exposed under the same conditions as the test specimens. If the fabric or yarn to be tested has been treated with some form of insecticide for the purpose of increasing its resistance to insect pests, 4 specimens of the same fabric or yarn untreated, should be exposed for comparison, if possible.

NOTE: The standard fabric may be purchased from the Chairman, Research Committee of the American Association of Textile Chemists and Colorists, Lowell Textile Institute, Lowell, Massachusetts.

TEST INSECTS

1. Larvae of the black carpet beetle (*Attagenus piceus* Oliv.) shall be used and should be 5 months old when put on test. Other species of fabric pests may be used for the purpose of obtaining additional information.

2. Ten larvae shall constitute the standard number of insects per test.

TEST CONDITIONS

1. Each test specimen or control shall be freed from any loosely adhering dirt or dust, then placed in a shallow, well-ventilated container such as a Petri dish, tin salve box, or some other suitable cage. The larvae shall be placed on the surface of the test specimen in the container after which the container shall be covered with non-wool cloth or a fine-mesh screen cover. Alternatively, the test specimen may be placed upon a backing plate of glass or metal, the larvae placed on the surface, and the whole covered with an inverted clear glass or plastic crucible with a perforated bottom.

2. The containers holding the test specimens shall be incubated for 28 days at a temperature of 80°±5° F. and a relative humidity of 60%±5% and tested by either of the methods given, i.e., Excrement Weight, Fabric Loss or Visual Damage.

PROCEDURE

At least 4 test specimens with ten larvae each of the black carpet beetle shall be prepared and exposed as explained above under "test conditions."

EXAMINATION

(a) The extent of the damage to the specimens of fabric or yarn shall be determined by visual examination, quantity of excrement deposited, and the number of larvae remaining alive.

(b) In the visual examination, the following evidence of damage shall be looked for:

2. Shearing of fibers.

NOTE: In the case of carpets where size is present on the back, the examination and reporting of damage shall be confined to the pile.

(c) The quantity of excrement deposited shall be dtermined by freeing it from all loose fibers, cast skins or exuvae and larvae, and weighing. This may be accomplished by removing the test fabric from the container, holding it over a piece of glazed paper, grasping it on opposite sides and pulling bacsk and forth btween the hands until all loose material, excrement, and larvae are transferred to the paper. In the case of pile fabrics and yarns, it is advisable to tap the back of the specimen to free it from all adhering excrement. Any loose residue in the container after the removal of the specimen should also be transferred to the glazed paper. The material collected on the paper shall then be transferred to a No. 3 Gooch Crucible,

EXCREMENT WEIGHT METHOD

For High Pile Fabrics, Feathers and Loose Fibers

This is the standard method previously published as the Tentative Method of Test. It is not suitable when tests are to be made with the webbing clothes moth. The webbing clothes moth has been found to react to various chemicals in a different way from the black carpet beetle, and where the webbing clothes moth is to be used, the fabric loss method should be used. (See page 239.)* It is only applicable for high pile fabrics, feathers and loose fibers. In all other instances, the visual damage shall act as the criterion of attack. A device known as a Visualometer shall be used to determine the amount of visual damage. The specimens shall be examined under a standard lighting set up similar to that shown in Fig. 1.

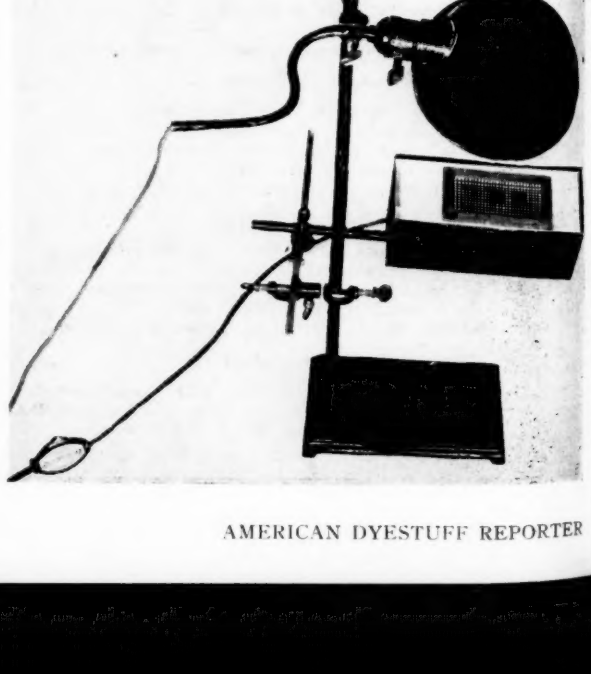


Fig. 1

* Year Book.

and by repeated tapping of the crucible, the excrement shall be sifted through the perforations into a suitable dish, and finally weighed on an analytical balance to the nearest 0.1 mg. For the purposes of this test, all material which sifts through the perforations of the Gooch crucible shall be construed as excrement.

VISUAL EXAMINATION

This examination shall be based on the Visualometer readings (Fig. 1). Place the sample after testing for the 28-day period and one of the original fabrics before testing on the squares marked on the ground glass cover. Over these samples place the Visualometer, and illuminate with the 10 W lamp under the glass in the box. The light shining through the samples makes it possible to count the squares, estimating to the nearest ¼ square damage by cut threads and holes (determined on one side only). After recording this damage, extinguish the 10 W lamp in the box and illuminate the sample by means of the 30 W lamp in the reflector adjusting the distance from the lamp to the surface for the best light conditions (approx. 8½ inches). All surface clipping and shearing of nap can now be determined. This evaluation to be made on both sides of the test sample and reported in per cent. When the readings of clipping and surface feeding have been made on both sides, divide the results by 2 to get the per cent clipping (for 1 sq. in. specimen).

VISUALOMETER—(Fig. 1)

This instrument consists of a metal frame ½" x 1/16" with a 2" x 4" opening. This frame contains small holes drilled (close to the inner edge) every 1/10" apart and strung with suitable wire or fiber thread, so that each square in the frame is equivalent to 1% on a 1 sq. in. surface.

REPORT

(a) The evidence of damage, the number of larvae remaining alive, and the weight of the excrement in milligrams shall be reported for each specimen of the treated sample and for the untreated control specimens.

(b) In the absence of visual damage, the specimen shall be considered satisfactorily resistant to carpet beetles if a quantity of excrement not over 6 mg. is deposited by the larvae, provided that under the same conditions a quantity of more than 15 mg. of excrement is deposited on the control specimens. It shall be understood that this statement applies only to the moth resistance of the specimen under the conditions of the test.

FABRIC LOSS METHOD

This method must be used when the webbing clothes moth is employed as the test insect, and may be used for the black carpet beetle, when comparative tests are being made with both insects, or when the operator prefers the technique and results of this test in individual laboratories but not for inter-laboratory results.

TEST INSECTS

Species—The black carpet beetle, Attagenus piceus Oliv., and the webbing clothes moth. Tineola bisselliella Hum., are recommended for testing as representative species of these two most common types of fabric pests. The black carpet beetle larvae should be 5 months old, while webbing clothes moth larvae should be 25 to 27 days old at the time of resting. Other species of fabric pests may be used for the purpose of obtaining additional information.

Number of Test Insects—Ten larvae of a given species shall constitute the standard number of insects per test.

Test Cages—Any shallow screen,—or non-wool cloth covered type of metal or glass container large enough to permit the test insects to be either in contact with or off the test specimen should be used. This type of cage allows for good ventilation of the test specimen and freedom of movement of the test insects.

Testing Conditions—Ideally all tests should be conducted in a dark location of a laboratory room where the temperature is 80° F.±5° and the humidity 60%±5%. Weights of test specimens may be secured by placing them in open weighing bottles in a desiccator and allowing them to remain there over night before each weighing. The humidity in the desiccator should be regulated to approximately 70% by placing a saturated NaCl solution in the bottom. Upon removal of specimens from the desiccator the weighing bottles should be closed immediately so that the outside humidity will have as little effect on the samples as possible.

TESTING PROCEDURE FOR WEIGHT LOSS TO BE USED IN INDIVIDUAL LABORATORIES ONLY

General Considerations—After weighing all specimens to the nearest 0.2 mg., they are placed in the cages along with 10 insects, and allowed to feed for 28 days. At the end of the test period all the specimens are cleaned of all excrement and clipping, again weighed, and the loss in fabric weight determined according to directions in paragraph (b). In addition 4 so-called "humidity check" specimens should be run in conjunction with the specimens under test. The "humidity checks" are quite important in this test procedure since they permit the adjustment of variations in the weight of the test specimens due to humidity changes. When tests are being conducted on fabric types other than on the standard Botany broadcloth, similar feeding and humidity checks must also be run.

Determination and Reporting of the Results—The extent of the damage to the test specimens by fabric pests should be determined on the excrement weight, visual evidences of damage, loss in weight of the test specimens and the per cent mortality of the test insects.

(a) *Visual Examination* of the test cloth should be made and evidences of damage reported according to:

(1) (W) feeding—cutting of fibers, resulting in holes in specimen

(2) nap (N) feeding—surface feeding or shearing of nap or pile

As a suggestion, visual evidences of feeding may be estimated in per cent of total amount eaten, for example, N-50% and W-10%. In cases of specimens where sizing is present on the back, the examination shall be confined to the pile.

(b) *The Loss in Weight of the Test Cloth* (after freezing from cast skins, excrement, etc. as directed under excrement weight method) due to the actual feeding of the test larvae as affected by humidity changes may be determined by the following formula:

$$L = A\frac{(C)}{(B)} - D$$

Legend:

- A equals—Average weight of 4 test specimens before testing
- B equals—Average weight of 4 humidity checks before testing
- C equals—Average weight of 4 humidity checks after testing
- D equals—Average weight of 4 test specimens after testing
- L equals—Adjusted loss in weight of test specimens due to insect feeding.

This formula is applicable to data in which humidity checks either gain or lose weight. See Table I for example.

Due to variable humidity conditions it is imperative that the weighings of test specimens and "humidity checks" be made as closely together as possible.

For satisfactory resistance to insect pests, test specimens using the standard test

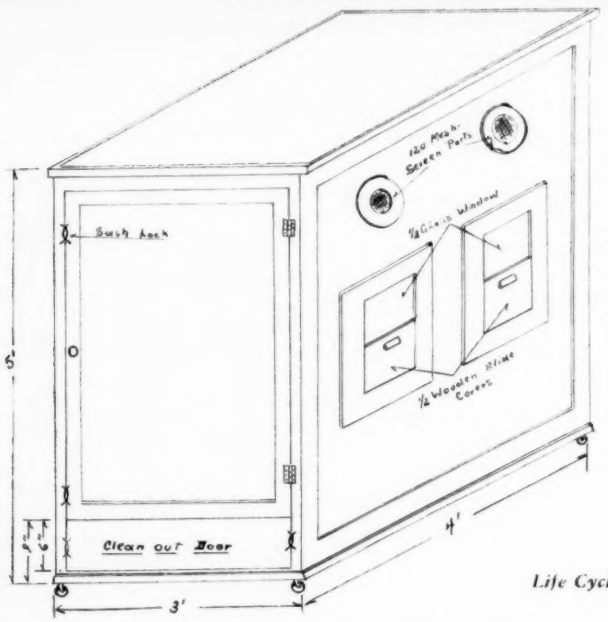
TABLE I

Table Showing Example of a Method of Calculating Fabric Weight Loss

Cloth	*Average Wt. of 4 Cloth Specimens* *Weight in mg. before test*	*Weight in mg. after test*	*Adjusted wt. loss in mg*
Test (specimens with larvae) ...	281.4	279.5	1.1
Humidity check (specimens without larvae).....	276.3	275.5	—

$$L = A\frac{(C)}{(B)} - D = \frac{(281.4 \times 275.5)}{276.3} - 279.5$$

$L = 1.1$ mg.



Life Cycle Cabinet

fabric must not show an average loss in weight of more than 8 mg. providing the loss in weight in the "feeding checks" averages 30 mg. or more.

Mortality counts are very important when testing the stomach poison types of fabrics pest deterrents. However, they are not so imperative when testing repellents. In any event, mortality percentages should be recorded since they are important in demonstrating the vitality of the test insects.

LIFE CYCLE METHOD

As a final criteria on the efficiency of a mothproofing compound, a life cycle incubation test is being considered. Specifications for a suitable cabinet are outlined below:

This is the life cycle cabinet built of plywood or other suitable material on a 1 x 2 frame, 5 ft. high, 3 ft. wide and 4 ft. deep.

8" from the bottom is placed a frame covered with chicken wire.

In parallel three inches from the top, four inches apart are ¼" rods for hanging the samples.

On both sides are wire covered parts for temperature and humidity control. Temperature — 80°±5° — Relatively humidity—60%±5%.

Windows with sliding covers are also cut into both sides for observation purposes while tests are being run without the necessity of opening the door of the cabinet.

Under the wire screen is placed approximately 2 pounds of clean wool.

CHARGING CABINET WITH INSECTS

12000±webbing cloths moth adults and 5000± black carpet beetle adults are placed in the cabinet after the samples to be tested are in position.

At the end of three months, the cabinet is opened, examined for infection, and another 12000±webbing cloths moths and 5000±black carpet beetle adults added.

At the end of the next three months period, the test samples are removed, sterilized by heat and examined for damage. To insure against the escape of insects from the cabinet, seal all door joints with scotch tape.

A TENTATIVE PROCEDURE FOR REARING AND HANDLING THE BLACK CARPET BEETLE*

The black carpet bettle cultures are maintained so that the age of each individual is known within the range of one week. The larvae are reared on a medium of dog food (Gaines Meal, Gaines Food Co., Inc., Sherburne, New York), ground so that it will pass through a 30-mesh sieve. A portion of the stock is set aside regularly for reproductive purposes. When pupation begins in this stock at about 8 months of age, it is examined once a week for pupae. This examination is made by sieving the whole culture of a 24-mesh sieve. The larvae, pupae, and the cast skins are retained on the sieve and the dog food medium passes through. The cast skins are blown off the sieve by means of the air current from an electric hair drier. The pupae are separated from the larvae by successively transferring from one sieve to another. At each transfer some of the larvae cling to the screen. After a number of such transfers all of the pupae will remain along with some of the larvae. The remaining larvae may be removed by hand sorting aided by their negative response to light.

The pupae thus collected are placed aside in a container for one week. The adults from 20 cc. of pupae will produce about 10,000 larvae from one week's oviposition. The following week the adults which have emerged from the pupae are placed on a 24-mesh sieve and the cast pupal skins blown from them by the air current of the hair drier. The adults are then cleaned to ensure freedom from mite infestation. This is done by placing them in a pint jar along with a half-pint of heat-sterilized ground dog food. They are then mixed thoroughly withthe dog food by rotating the container. The dog food is sieved off, carrying any mites or mite eggs with it. This procedure is repeated with a second portion of sterile food medium to ensure complete removal of the mite infestation.

For oviposition, the adult beetles from 20 cc. of pupae are placed in a pint jar which is loosely filled with 1.5-inch squares of supplemented wool filter cloth. This cloth is supplemented by spraying with an aqueous extract of brewers yeast until well moistened on both sides, after which it is permitted to dry. The extract of brewers yeast for this purpose is prepared by grinding brewers yeast powder with water in a ball mill for at least 12 hours, in the proportion of 1 gram of yeast powder to 10 cc. of water. After grinding in this way, the extract is centrifuged or filtered and the resultant clear liquor used for supplementing the wool. Because the eggs are left on the oviposition cloths for hatching it is important that this supplement be provided on the cloths to supply the young larvae with a more satisfactory diet.

After one week of oviposition on the supplemented cloths, the adults are removed. They may be re-established for a second week of oviposition on fresh cloths or they may be discarded. The egg production during the second week is much reduced in comparison with that of the first week.

The cloth squares on which the eggs have been deposited are set aside for hatching. The eggs of the black carpet bettle, unlike those of the webbing clothes moth, are too fragile to be removed from the cloths without injury. Three weeks after the removal of the adults, the larvae have hatched from the eggs and are developed sufficiently to be handled without injury and to be seen readily with the naked eye. At this time, they are removed

* This procedure is contained in a paper published by—Ralph E. Heal, Rutgers University, New Brunswick, N. J.

from the oviposition cloths by gentle tapping and brushing with a camel's hair brush onto a tray from which they are counted into pint jars full of ground dog food as a rearing medium. One pint of dog food is sufficient for the rearing of 1000 larvae for four months. The jars are closed with a filter paper held in place by screw-type closure rim. When the larvae reach the age of four months the old food is removed by sieving, the cast skins are blown away, and the larvae are re-established on fresh food. When the larvae retained for reproduction reach the age of eight months, they are again provided with fresh food.

In practice, all of the above listed steps are carried out once a week and a constant supply of developing stock is maintained. Cultures providing over 10,000 larvae per week for testing can be maintained under this system with about 6 to 8 hours of labor per week.

A TENTATIVE PROCEDURE FOR REARING AND HANDLING THE WEBBING CLOTHES MOTH*

The following suggestions are offered as a tentative procedure for rearing the webbing clothes moth, *Tineola bisselliella Hum.*

REARING CONTAINERS

Wide-mouth glass jars of quart or half-gallon size are suggested. The flat lid is replaced by filter paper and held in place by the ring or the lid. Other types of container of similar size are satisfactory.

OVIPOSITION CAGE

A one-gallon paint bucket with the following modifications is suggested: A section is cut about 2" x 5" from the bottom or side and 16-mesh screen is soldered over it. This opening is covered with wool cloth and held in place by strings or rubber bands. A circle slightly smaller than a ring from a wide-mouth rearing jar is cut in the lid and the ring is soldered to the lid. A jar turned into the ring will close this opening. A ½-inch hole should be cut near the edge of the lid and fitted with a cork.

REARING MEDIUM

About ½ teaspoonful of autoclaved dry brewer's yeast with about 20 grams of wool cloth is recommended.

INSECTARY REARING CONDITIONS

A temperature of 80±5° F. and relative humidity of 60%±10% is recommended. Other conditions may be satisfactory, but the time for development of the insects will vary.

MAINTENANCE OF CULTURE

Adults in mature cultures are transferred to the oviposition cage either by suitable suction apparatus or by screwing culture jars into the ring on the lid of the oviposition cage and placing a light behind it. Eggs are deposited on the wool cloth over the screened opening and these should be collected in four days or less to avoid complications due to hatching. This is done by removing the cloth and shaking and brushing it into a dry tray. Gentle air currents remove the lint and the eggs are poured over a 60-mesh screen to remove any mite eggs that may be present. The clothes moth eggs are examined under magnification and any living predaceous forms are removed. The cleaned eggs are then measured in a centrifuge tube and a ratio of 0.2 ml. per 20 or 30 grams wool is recommended. The eggs are scattered on the wool cloth and the dry brewer's yeast is sprinkled over them. The strips of wool are rolled up and held together by strings or rubber bands. The size of roll should be such that it fits easily into the rearing container.

Larvae are ready for test about 25 to 27 days after starting the culture. If the roll of fabric is carefully unrolled on a tray near a low wattage light, larvae can be transferred to test fabrics easily and without injury by means of low tension forceps. Larvae not used for test purposes are allowed to mature and the adults are used to continue the culture.

* Method proposed by A. H. Goddin.

EVALUATION OF COMPOUNDS

Designed to Increase the Resistance of Fabrics and Yarns to Insect Pests*

Tentative Method

SCOPE

1. This method of test covers the procedure for the evaluation of compounds or treatments designed to protect textiles from damage by insect pests such as moths or carpet beetles. It comprehends not only the initial protection furnished by the treatment in question, but also the permanency of this protection during conditions of ordinary use.

TEST SPECIMENS

2. The compound to be tested shall be applied in any desired concentration to a standard sample of pure undyed wool† or to any special fabric which is of particular interest. After treatment the specimen should be thoroughly aired for a period of 7 days for the removal of all volatile constituents.

PROCEDURE

3. The resistance of the treated fabric to insect pests shall be determined according to A.A.T.C.C. Test "Tentative Method of Test for Evaluation of Fabric Pest Deterrents," both immediately after the treatment and airing specified in section 2 above, and after subjecting it to any or all of the following use tests, as desired:

(a) *Duration.*—The procedure specified in A.A.T.C.C. Test "Tentative Method of Test for Evaluation of Fabric Pest Deterrents" shall be continued for the determination of the length of time that the treatment in question will impart protection from insect pests. The specimen shall be examined for visual evidences of damage after each 28 day period of exposure. If no evidences are present, the number of active larvae shall be brought back to 10 and the test continued.

(b) *Washing.*—The treated specimen shall be washed according to the procedure described below, and the washing shall be repeated up to 5 times as desired.

Procedure: The test is to be run for 5 minutes at 95°. F in a soap solution containing 0.5% natural chip soap, using a bath length of 30 times as much water as fabric. The sample after running in this soap solution shall be rinsed twice in water approximately 85° F. using the same dilution of water as in the washing, that is 30/1. For grade of soap in this washing test, please see page 174, 1944 Year Book, entitled "Group W—Fastness Tests for Dyed Wool."

(c) *Cleaning.*

(1) *Dry with Stoddard Solvent.*—The treated specimen shall be cleaned with Stoddard Solvent according to the procedure described in Commercial Standard CS59-41, paragraph 18a, with the omission of the 4 parts of water from the cleaning solution. The cleaning shall be repeated up to 5 times as desired.

(2) *Dry with Perchlorethylene.*—The Stoddard Solvent in the cleaning solution specified for (1) shall be replaced by Perchlorethylene. The cleaning procedure shall be repeated up to 5 times as desired.

* This test has been formulated jointly with the Committee D-13 of the American Society for Testing Materials, and the Committee on Mothproofing of the National Association of Insecticide and Disinfectant Manufacturers.

† NOTE: A standard fabric of this type may be purchased from the Secretary of the American Association of Textile Chemists and Colorists, Lowell Textile Institute, Lowell, Massachusetts.

(3) *Wet.*—Duplicate specimens after each cleaning according to (1) or (2), shall be further cleaned according to the procedure described in Commercial Standard CS59-41, paragraph 18b.

(d) *Hot Pressing.*—The treated specimen shall be pressed by hand according to the procedure described in Commercial Standard CS59-41, paragraph 19a. The pressing shall be repeated up to 5 times as desired.

(e) *Light.*—The treated specimen shall be exposed to light in the Fade-Ometer, according to the procedure described in A.A.T.C.C. Test "Fastness to Light of Textiles," (page 185) for periods ranging from 10 to 40 hours as desired.

(f) *Abrasion.*—The treated specimen shall be subjected to 2,000 revolutions of the carpet wear test machine according to the procedure described in Research Paper RP640, National Bureau of Standards Journal of Research, Vol. 12, pages 155-156 (1934).

(g) *Sea Water.*—The treated specimen shall be subjected to the sea water test according to the procedure described in A.A.T.C.C. Test "Fastness to Sea Water." The test shall be repeated up to 5 times as desired.

(h) *Perspiration.*

(1) *Acid.*—The treated specimen shall be tested with the acid perspiration solution according to the procedure described in A.A.T.C.C Test "Fastness to Perspiration of Dyed Textiles." The test shall be repeated up to 5 times as desired.

(2) *Alkaline.*—The treated specimen shall be tested with the alkaline perspiration solution according to the procedure described in A.A.T.C.C. Test "Fastness to Perspiration of Dyed Textiles." The test shall be repeated up to 5 times as desired.

NOTE: Tests are being developed to determine the effect upon the treated specimen of sponging, soil and urine. It is planned to include such tests in a later revision of this method.

CLASSIFICATION

4. The classification of the permanency of the protection furnished by compounds designed to increase the resistance of fabrics and yarns to insect pests shall be based upon comparison of the results obtained in A.A.T.C.C. "Method of Test for Evaluation of Fabric Pest Deterrents" before and after the use tests specified in Section 3 above. The following classes shall be provided for the tests specified in paragraphs 3 (b), 3 (c), 3 (d), 3 (g) and 3 (h):

Class 0.—Appreciable change in the resistance of the treated specimen to insect pests after 1 test.

Class 1.—No appreciable change in the resistance of the treated specimen to insect pests after 1 test, but appreciable change after 2 tests.

Class 2.—No appreciable change in the resistance of the treated specimen to insect pests after 2, 3, or 4 tests, but appreciable change after 5 tests.

Class 3.—No appreciable change in the resistance of the treated specimen to insect pests after 5 tests.

The following classes shall be provided for the test specified in paragraph 3 (e):

Class 0.—Appreciable change after 10 hours' exposure in the Fade-Ometer.

Class 1.—No appreciable change after 10 hours but appreciable change after 20 hours.

Class 2.—No appreciable change after 20 hours but appreciable change after 40 hours.

Class 3.—No appreciable change after 40 hours exposure.

The following classes shall be provided for the test specified in paragraph 3 (f):

Class 0.—Appreciable change in the resistance of the treated specimen in insect pests after 2,000 revolutions of the carpet wear test machine.

Class 3.—No appreciable change in the resistance of the treated specimen to insect pests after 2,000 revolutions of the carpet wear test machine.

REPORT

5. The report shall include a designation of classification of the treated specimen with respect to the change in its resistance to insect pests after each of the use tests specified in Section 3, with the exception of paragraph 3 (a). The result of the duration test specified in paragraph 3 (a) shall be reported as the number of days required to develop visual evidences of damage to the treated specimen.

NOTE: The selection of the particular use tests to be applied to the specimen in question should be governed by the use to which the fabric is to be put. It is anticipated that various organizations will shortly be contacted with the idea of selecting the test procedures which best suit the requirements of each class of wool goods and specify the classification to be used.

—♦ ♦—

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M. Oleta Shows—Chemist, E. I. duPont de Nemours & Co., Inc., Technical Lab., Wilmington, Del. Sponsors: C. A. Seibert, C. A. Sylvester.

MEETING, PHILADELPHIA SECTION

THE October 19th meeting of the Philadelphia Section will be held at the Bellevue Stratford, Broad and Walnut Sts., Philadelphia.

The speaker of the evening will be Prof. Harvey A. Neville, head of the Department of Chemistry and Chemical Engineering, and Chairman of the Executive Committee of the Engineering College, Lehigh University. His subject will be "Emulsions and Their Applications to Textiles."

MEETING, NEW YORK SECTION

AT the meeting of the New York Section to be held on October 19th at the Downtown Athletic Club, 19 West Street, New York City, the first two speakers will be Werner von Bergen of Forstmann Woolen Company and Frank S. Richardson of the Waldrich Company. The speakers are members of the textile team that investigated conditions in Germany and they will supplement the information which they presented at the October 2nd meeting sponsored by the Inter-Society Council for Textile Research.

The second two speakers, Arthur Wachter of American Viscose Corp. and C. Wilcock, Chief Chemist of the Droylsden Plant of Cortaulds Ltd. in England, will discuss the application of resins. Mr. Wachter recently returned from an extended trip in Europe, representing the American Viscose Corp., and he will report on what he observed. He spent considerable time with Mr. Wilcock at the Droylsden plant and is in a position to present a comprehensive review. Mr. Wilcock is an authority on resins and their application.

MEETING, RHODE ISLAND SECTION

A MEETING of the Rhode Island Section will be held on October 26th at the Hall of the Providence Engineering Society, 195 Angell Street, Providence, R. I. Speakers will be: R. W. Jacoby, Ciba Co., Inc., "Some Aspects of Vat Dyeing," and O. W. Clark, Calco Chemical Division, American Cyanamid Co., "Some Fundamental Principals of Vat Dyeing."

MEETING, NORTHERN NEW ENGLAND SECTION

A MEETING of the Northern New England Section will be held on October 19th at the Hotel Manger, Boston, Mass. Professor Edward R. Schwarz, in charge of Textile Technology at the Massachusets Institute of Technology, will speak on "Electronics in Textile Testing."

CALENDAR OF COMING EVENTS

Meeting, Piedmont Section, Hotel Charlotte, Charlotte, N. C., October 13, 1945. Election of officers will be held.

Meeting, New York Section, Downtown Athletic Club, New York City, October 19, 1945.

Meeting, Philadelphia Section, October 19, 1945.

Meeting, Northern New England Section, Hotel Manger, Boston, Mass., October 19, 1945.

Meeting, Rhode Island Section, October 26, 1945

NOTICE TO SECRETARIES OF LOCAL SECTIONS:

Please advise the National Secretary or the American Dyestuff Reporter of your meeting dates for the 1945-1946 season as soon as available.

Lapel buttons, at $1.50 each, may be purchased, by members in good standing, from the Secretary.

Wool Protein Behavior—

(*Continued from Page 398*)

Neutral amino acids—

1. $NH_2.R.COOH \rightleftharpoons NH_2.R.COO^- + H^+$
2. $H_2O + NH_2.R.COOH \rightleftharpoons {}^+NH_3.R.COOH + OH^-$

Acid amino acids—

1. $HOOC.R.CH.COOH \rightleftharpoons HOOC.R.CH.COO^- + H^+$ (NH₂ / NH₂)
2. $HOOC.R.CH.COO^- \rightleftharpoons {}^-OOC.R.CH.COO^- + H^+$ (NH₂ / NH₂)
3. $H_2O + HOOC.R.CH.COOH \rightleftharpoons HOOC.R.CH.COOH + OH^-$ (NH₂ / NH₃⁺)

Basic amino acids—

1. $NH_2.R.CH.COOH \rightleftharpoons NH_2.R.CH.COO^- + H^+$ (NH₂ / NH₂)
2. $H_2O + NH_2.R.CH.COOH \rightleftharpoons {}^+NH_3.R.CH.COOH + OH^-$ (NH₂ / NH₂)
3. $H_2O + {}^+NH_3.R.CH.COOH \rightleftharpoons {}^+NH_3.R.CH.COOH + OH$ (NH₂ / NH₃⁺)

CLASSICAL DISSOCIATION CONSTANTS

The mass law expressions for the preceding reactions have been simplified by letting N equal the whole neutral amino acid molecule; when N is qualified by a positive or negative charge, the correspondingly charged molecule is indicated. Similarly, A stands for the acid amino molecule, and B for the basic amino acid molecule, which are likewise modified in some cases.

1. $\dfrac{[N^-]\ [H^+]}{[N]} = k_a$ 2. $\dfrac{[N^+]\ [OH^-]}{[N(H_2O)]} = k_b$

1. $\dfrac{[A^-]\ [H^+]}{[A]} = k_a$ 3. $\dfrac{[A^+]\ [OH^-]}{[A(H_2O)]} = k_b$

2. $\dfrac{[{}^-A^-]\ [H^+]}{[A^-]} = k_a'$

1. $\dfrac{[B^-]\ [H^+]}{[B]} = k_a$ 2. $\dfrac{[B^+]\ [OH^-]}{[B(H_2O)]} = k_b$

3. $\dfrac{[{}^+B^+]\ [OH^-]}{[{}^+B(H_2O)]} = k_b'$

ZWITTERION FORMULATION OF THE DISSOCIATION OF AMINO ACIDS (BJERRUM)

In the equations which follow, the order in which the different groups dissociate was selected arbitrarily, but the net charge would remain unaffected if a different choice were made. Michalis[34] explains why a charged molecule is considered as the undissociated form in these reactions.

Neutral amino acids—

1. $^+NH_3.R.COOH \rightleftharpoons {}^+NH_3.R.COO^- + H^+$
2. $H_2O + NH_2.R.COO^- \rightleftharpoons {}^+NH_3.R.COO^- + OH^-$

Acid amino acids—

1. $HOOC.R.CH.COOH \rightleftharpoons HOOC.R.CH.COO^- + H^+$ (NH_3^+ / NH_3^+)
2. $HOOC.R.CH.COO^- \rightleftharpoons {}^-OOC.R.CH.COO^- + H^+$ (NH_3^+ / NH_3^+)
3. $H_2O + {}^-OOC.R.CH.COO^- \rightleftharpoons {}^-OOC.R.CH.COO^- + OH^-$ (NH_2 / NH_3^+)

Basic amino acids—

1. $^+NH_3.R.CH.COOH \rightleftharpoons {}^+NH_3.R.CH.COO^- + H^+$ (NH_3^+ / NH_3^+)
2. $H_2O + NH_2.R.CH.COO^- \rightleftharpoons {}^+NH_3.R.CH.COO^- + OH^-$ (NH_2 / NH_3^+)
3. $H_2O + {}^+NH_3.R.CH.COO^- \rightleftharpoons {}^+NH_3.R.CH.COO^- + OH^-$ (NH_2 / NH_3^+)

Zwitterion dissociation constants.

1. $\dfrac{[{}^+N^-]\ [H^+]}{[N^+]} = K_A$ 2. $\dfrac{[{}^+N^-]\ [OH^-]}{[{}^-N(H_2O)]} = K_B$

1. $\dfrac{[{}^+A^-]\ [H^+]}{[A^+]} = K_A$ 3. $\dfrac{[{}^-\overset{+}{A}\,]\ [OH^-]}{[{}^-A^-(H_2O)]} = K_B$

2. $\dfrac{[{}^-\overset{+}{A}{}^-]\ [H^+]}{[{}^+A^-]} = K_A'$

1. $\dfrac{[{}^+\overset{-}{B}{}^+]\ [H^+]}{[{}^+B^+]} = K_A$ 2. $\dfrac{[{}^+B^-]\ [OH^-]}{[B^-(H_2O)]} = K_B$

3. $\dfrac{[{}^+\overset{-}{B}{}^+]\ [OH^-]}{[{}^+B^-(H_2O)]} = K_B'$

ACID CONCEPT FORMULATION OF THE DISSOCIATION OF AMINO ACIDS (BRONSTED)

In order that the Bronsted equations may all express dissociation in terms of splitting off a hydrogen ion, the undissociated form is considered to be that carrying the greatest possible positive charge.

Neutral amino acids—

1. $^+NH_3.R.COOH \rightleftharpoons {}^+NH_3.R.COO^- + H^+$
2. $^+NH_3.R.COO^- \rightleftharpoons NH_2.R.COO^- + H^+$

Acid amino acids—

1. $HOOC.R.CH.COOH \rightleftharpoons HOOC.R.CHCOO^- + H^+$ (NH_3^+ / NH_3^+)
2. $HOOC.R.CH.COO^- \rightleftharpoons {}^-OOC.R.CH.COO^- + H^+$ (NH_3^+ / NH_3^+)
3. $^-OOC.R.CH.COO^- \rightleftharpoons {}^-OOC.R.CH.COO^- + H^+$ (NH_3^+ / NH_2)

Basic amino acids—

1. $^+NH_3.R.CH.COOH \rightleftharpoons {}^+NH_3.R.CH.COO^- + H^+$ (NH_3^+ / NH_3^+)
2. $^+NH_3.R.CH.COO^- \rightleftharpoons {}^+NH_3.R.CH.COO^- + H^+$ (NH_3^+ / NH_2)
3. $^+NH_3.R.CH.COO^- \rightleftharpoons NH_2.R.CH.COO^- + H^+$ (NH_2 / NH_2)

Table 4

Classical dissociation constants (Hndbk. Chem. & Phys.)

25° C.	k_a	k_a'	k_b	k_b'	pk_a*	pk_a'	pk_b	pk_b'	$p\left(\frac{k_w}{k_b}\right)$**	$p\left(\frac{k_w}{k_b'}\right)$
Acetic Acid	1.86×10^{-5}				4.73					
Ammonium Hydroxide			1.8×10^{-5}				4.74		9.26	
Glycine	2.5×10^{-10}		2.2×10^{12}		9.6		11.66		2.34	
Aspartic Acid	2.2×10^{-4}	2.5×10^{-10}	7.5×10^{-13}		3.66	9.6	12.12		1.88	
Glutamic Acid	5.6×10^{-5}	2.2×10^{-10}	1.6×10^{-12}		4.25	9.66	11.8		2.2	
Tyrosine	7.0×10^{-10}	7.0×10^{-13}	1.7×10^{-13}		9.15	10.15	11.77		2.23	
Lysine	3.0×10^{-11}		8.9×10^{-6}	1.0×10^{-12}	10.52		5.05	12.0	8.95	2.0
Arginine	3.3×10^{-13}		1.1×10^{-5}	1.1×10^{-12}	12.48		4.96	11.96	9.04	2.04
Histidine	6.7×10^{-10}		1.0×10^{-9}	6.6×10^{-13}	9.17		8.0	12.18	6.0	1.82

	Zwitterion (Bjerrum) dissociation constants						*Acid (Bronsted) dissociation constants pK and probable determining group*†								
										peptide	*extra*	*peptide*	*extra*		
25°	pK_A	pK_A'	pK_B	pK_B'	$p\left(\frac{k_w}{K_B}\right)$	$p\left(\frac{k_w}{K_B'}\right)$	pK_1	pK_2	pK_3	*COOH*	*COOH*	—*OH*	—NH_2	—NH_2	=*NH*	≡*N*
Acetic Acid																
Ammonium Hydroxide																
Glycine	2.34		4.4		9.6		2.34	9.6		2.35			9.78			
Aspartic Acid	1.88	3.66	4.4		9.6		1.88	3.66	9.6	2.09	3.87		9.82			
Glutamic Acid	2.2	4.25	4.34		9.66		2.2	4.25	9.66	2.19	4.28		9.66			
Tyrosine	2.23	9.15	3.85		10.15		2.23	9.15	10.15	2.20		10.1	9.1			
Lysine	2.0		3.48	5.05	10.52	8.95	2.0	8.95	10.52	2.18			8.95	10.53		
Arginine	2.04		1.52	4.96	12.48	9.04	2.04	9.04	12.48	2.02			9.04	—12.48—		
Histidine	1.82		4.83	8.0	9.17	6.0	1.82	6.0	9.17							—6.10—

* pk = — log k (analogous to converting $[H^+]$ to pH).

** In order to express both of the values pk_a and pk_b in terms of one scale (pH), pk_b must become $p\left(\frac{k_w}{k_b}\right)$ from the following considerations:

$[H^+]\,[OH^-] = k_w = 1^{-14} \times 10^{-14}$ (dissociation of water)

$\frac{k_w}{[H^+]} = [OH^-]$, which under the condition $\alpha = \frac{1}{2}$, or 50%, $= k_b$

$\frac{k_w}{k_b} = [H^+]$ — $\log [H^+] = pH = p\left(\frac{k_w}{k_b}\right) = 14 - pk_b$

† Taken from D. Hitchcock, in C. Schmidt, Chem. of Amino Acids and Proteins, Chas. Thomas Co., Baltimore (1944) (2nd ed.) p. 613.

Bronsted dissociation constants

1. $\frac{[^+N^-]\,[H^+]}{[N^+]} = K_3$ | 2. $\frac{[N^-]\,[H^+]}{[^+N^-]} = K_2$

1. $\frac{[^+A^-]\,[H^+]}{[A^+]} = K_1$ | 3. $\frac{[^-A^-]\,[H^+]}{[^+A^-]} = K_3$

2. $\frac{[^-\overset{+}{A}^-]\,[H^+]}{[^+A^-]} = K_1'$

1. $\frac{[^-\overset{-}{B}^+]\,[H^+]}{[^+B^+]} = K_A$ | 2. $\frac{[^+B^-]\,[H^+]}{[^+B^+]} = K_2$

3. $\frac{[B^-]\,[H^+]}{[^+B^-]} = K_2'$

Basic amino acids

$K_A = \frac{k_w}{k_b'}$ | $K_B = \frac{k_w}{k_a}$ | $K_B' = k_b$

$K_1 = \frac{k_w}{k_b'}$ | $K_2 = k_a$ | $K_2' = \frac{k_w}{k_b}$

RELATIONSHIPS OF THE DISSOCIATION CONSTANTS

Assuming that the concentrations of a molecular species with equivalent net charges are equal in the different systems (for example,

$$[^-\overset{+}{A}^-] = [A^-],$$

the following relationships may be derived algebraically. That the assumption is valid follows from the consideration that all three systems are merely different interpretations of one set of phenomena.

Neutral amino acids

$K_A = \frac{k_w}{k_b}$ | $K_B = \frac{k_w}{k_b}$

$K_1 = \frac{k_w}{k_b}$ | $K_2 = k_a$

Acid amino acids

$K_A = \frac{k_w}{k_b}$ | $K_A' = k_a$ | $K_B = \frac{k_w}{k_a'}$

$K_1 = \frac{k_w}{k_b}$ | $K_1' = k_a$ | $K_2 = k_a'$

DISSOCIATION OF THE GROUPS WHICH MAY BE FREE IN WOOL

Figures 2-7 show the dissociation curves of the dibasic and diacid amino acids found in wool. Figure 8 shows the curves of the groups (Hitchcock's allocation) which may be free in wool, assuming the constants to remain unchanged under the new conditions.

The question may arise, why is it that all the curves do not face in one direction, since, according to Bronsted's scheme, all represent acid dissociation? The answer lies in that fact that the charged ampholyte (ampholytoid) is the compound being traced, and its state may be represented by the dissociation curve in some cases, and by its mirror image, the residue (ϱ)* curve,[35] in others. Inspection of the equilibrium equations shows that the dissociation curves of the extra groups in aspartic and glutamic acids, and tyrosine will represent the negative charge of the empholyte, while the residue curves of the extra groups in lysine, arginine, and histidine must be used to represent its positive charge.

* Dissociation residue $\varrho = 1 - \alpha$.

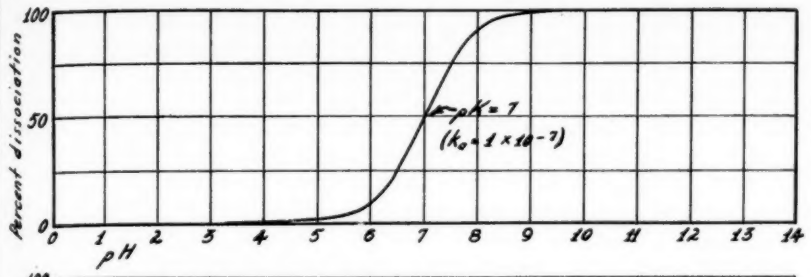

Figure 1. Dissociation of an Acid whose Dissociation Index = 1×10^{-7} as a Function of pH.

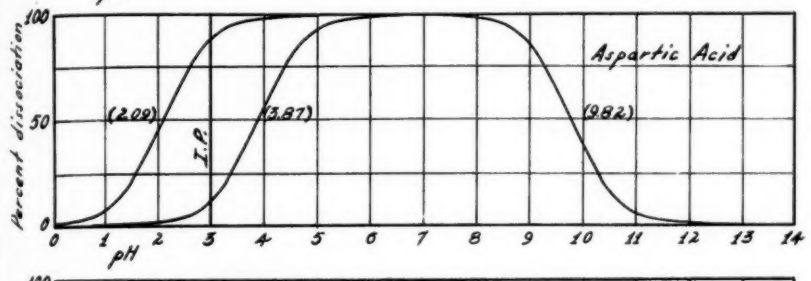

Figure 2. Dissociation Curves of Aspartic Acid.

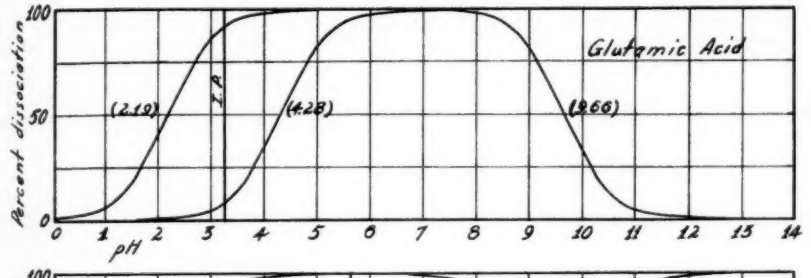

Figure 3. Dissociation Curves of Glutamic Acid.

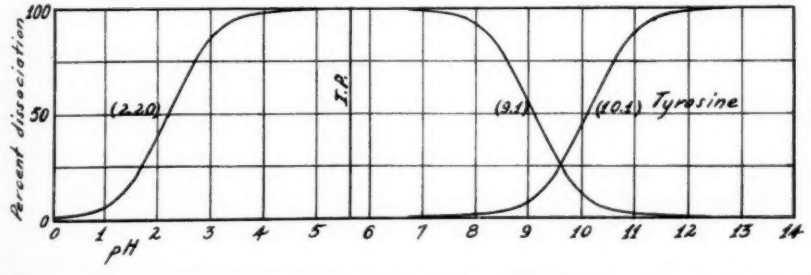

Figure 4. Dissociation Curves of Tyrosine.

DISSOCIATION DIAGRAM OF WOOL

If we take the dissociation curves of the extra polar groups of the dibasic and diacid amino acids which are found in wool and weight them according to their relative occurrence in the wool molecule, a composite picture of the dissociation of wool as an acid and a base can be drawn on the pH scale (Fig. 9).

Comparison of these dissociation curves with experimentally determined combination curves of wool with anions and cations shows the agreement to be extremely poor. However, the difference (ordinate) between the acid and basic dissociation gives curves which approximate experimental results much more satisfactorily. An easily reversible linkage between the acid and basic groups might explain this. The salt linkage theory postulated by Speakman (illustrated earlier in this paper) resulted from this consideration, and finds its main support in it. Whatever the cause, the difference curves appear to give a truer representation of the charge carried by wool over the pH range.

Even on theoretical grounds, the wool dissociation diagram cannot be considered to be better than a rough approximation for several reasons. Examination of the constants for the amino acids shows that the dissociation of the extra polar group is affected considerably by that of the other polar groups. It is reasonable to suppose that the dissociation of the extra groups will change when they are present in side chains of the protein molecule. While the case is not strictly analogous, some indication of the magnitude of the error in the assumption that the dissociation constants of the extra acid and basic groups can still be applied to them when the amino acids were bound in peptide linkage may be obtained from the following data[25]:

Compound	Acid Dissociation Constants		Basic Dissociation Constants		Isoelectric Points*
	ka	*pka*	*kb*	*pkb*	*pI*
Glycine	1.99×10^{-10}	9.70	2.6×10^{-12}	11.58	6.06
Di-peptide (glycyl-glycine)	0.63×10^{-8}	8.20	1.35×10^{-11}	10.87	5.66
Tri-peptide (di-glycyl-glycine)	1.0×10^{-8}	8.00	1.26×10^{-11}	10.90	5.55
Tetra-peptide (tri-glycyl-glycine)	1.78×10^{-8}	7.75	1.12×10^{-13}	10.95	5.40
Penta-peptide (tetra-glycyl-glycine)	2.0×10^{-8}	7.70	1.12×10^{-13}	10.95	5.38
Hexa-peptide (penta-glycyl-glycine)	2.5×10^{-8}	7.60	1.12×10^{-13}	10.95	5.32

* Discussed below.

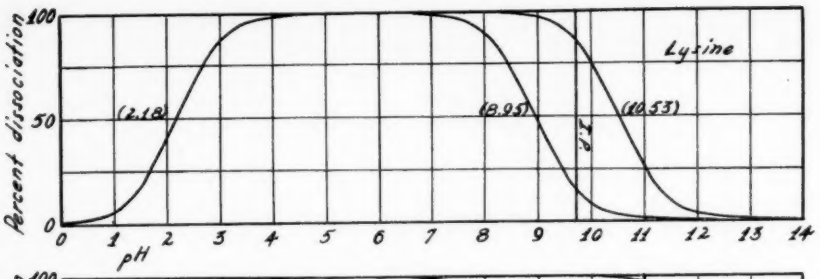

Figure 5. Dissociation Curves of Lysine.

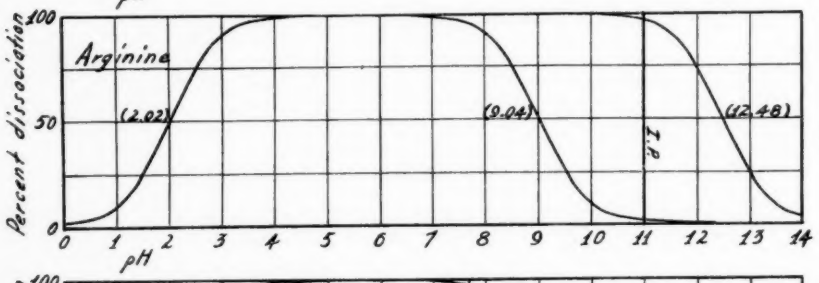

Figure 6. Dissociation Curves of Arginine.

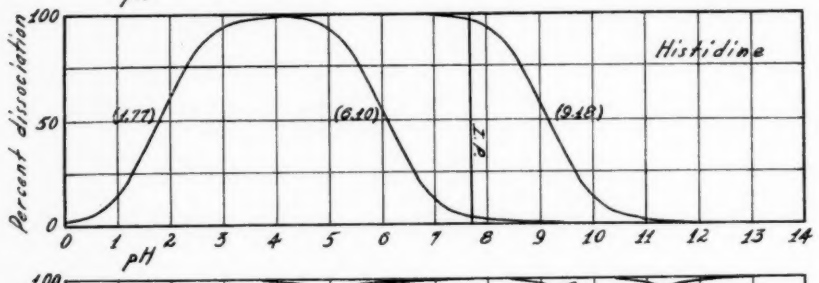

Figure 7. Dissociation Curves of Histidine.

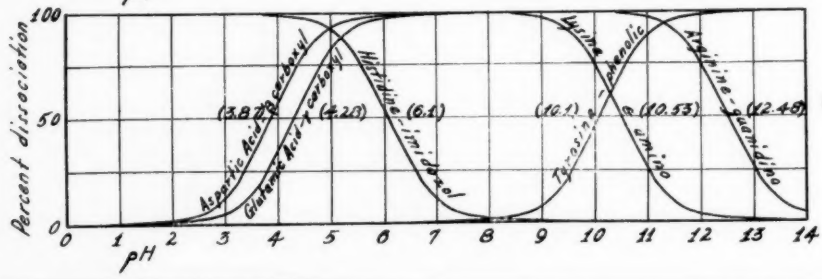

Figure 8. Dissociation of Groups Which May Be Free in Wool.

The trend of this data is in the direction of progressively less change, but its unqualified application to wool dissociation is perhaps inadvisable because the groups involved are all terminal groups.

A meaningful critical evaluation of the theoretical dissociation curves in Fig. 9 can scarcely be made without some idea of the empirical behavior of wool as a function of pH. Data appearing in the literature, and collected in this laboratory, indicate that a disturbingly large discrepancy exists between the difference curves and experimentally determined combination curves of wool with anion and cation.

Though random speculation suggests several compromises which would improve the agreement, most adjustments would lie outside the limitations set by the data with which we are working. Thus, a dissociation diagram which more nearly conforms to empirical data can be drawn if the weaker, rather than stronger, acid constants of aspartic and glutamic acids are allocated to the "free" groups (Fig. 10); however, such a selection finds but dubious support in considerations presented to this point. Also, a much improved representation could be drawn if both the acid and basic dissociation constants were shifted to lower pH values. An exception might be claimed for the idea that the acid amides may not be so inviolate under some working conditions as assumed: The empirical evidence that the true dissociation curves of wool lie somewhere between the limits set by curves drawn as if acid amides were present, and as if they were absent, seems sufficiently strong to justify presenting these curves in Figure 11.

The tentative, much qualified nature of the whole system should caution against too strict reliance upon any of the dissociation diagrams.

ISOELECTRIC POINTS

When a suspension of powdered wool is placed between the D.C. electrodes of an electrophoretic cell, the particles migrate toward the negative pole in (for example) a sufficiently acid solution, and toward the positive pole in alkaline solution. At some intermediate point or zone the average mobility is zero; this is an isoelectric point.[26]

Technical literature contains many references to the isoelectric condition of ampholytes and ampholytoids, which too often ignore necessary qualifications. It is obviously impossible to manipulate the hyrogen-ion concentration without introducing other ions besides H^+ or OH^-; in practice, it is necessary to add an acid, or base, or salt, or a combination to control this variable. It is also impossible to obtain an uncontaminated amphoteric

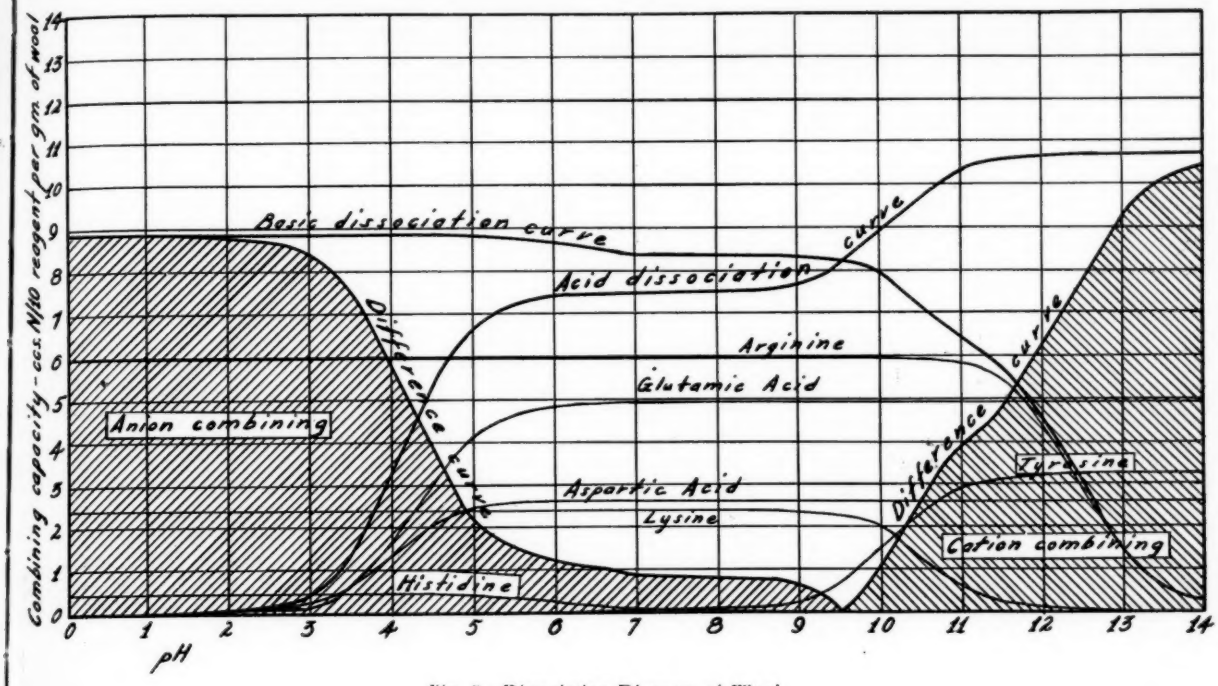

Fig. 9—Dissociation Diagram of Wool.

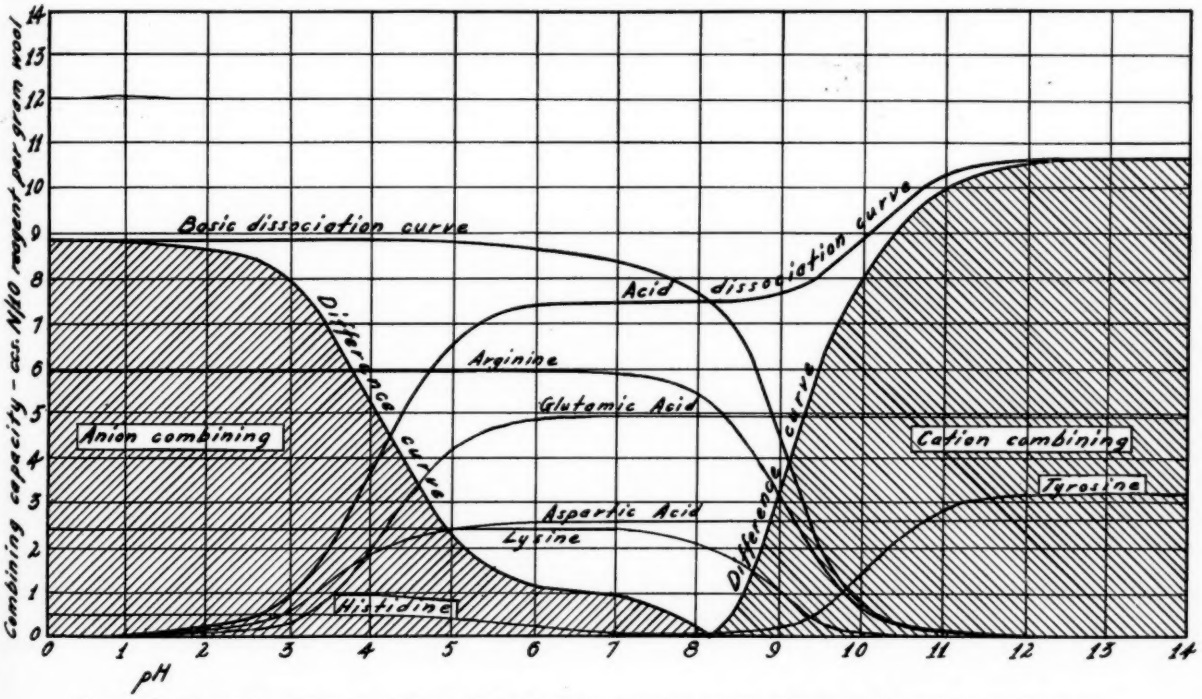

Figure 10. Dissociation Diagram of Wool if Weaker Basic Constants Are Used for Arginine and Lysine (See text).

body. The presence of ions other than H^+ or OH^- will shift an isoelectric point, unless by chance they affect the total positive and negative surface (effective) charges of the ampholyte or ampholytoid to the same extent. For example, Michaelis,[29] working with casein, found that of many salts tested only two, rubidium chloride and sodium acetate, caused no change in the pH of optimal flocculation, a point coinciding very well with the isoelectric condition measured by the transport method.[30]

If some or all of the acid groups in wool are inactivated by combination with a cation to form a relatively irreversible compound, the attraction of anions by the basic groups is greater at a given $[H^+]$,[28] and vice versa. This becomes significant when it is learned that much of the ash of wool consists of the oxides of

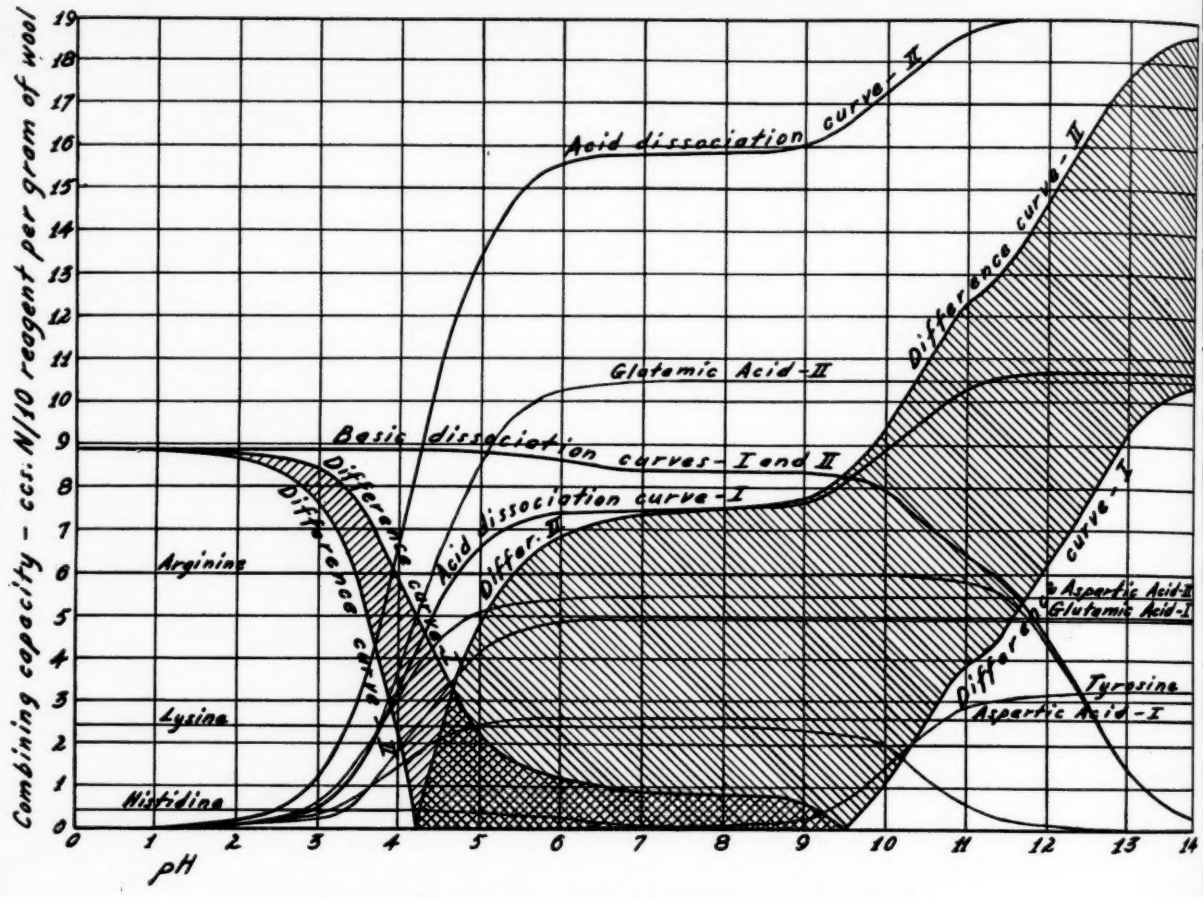

Figure 11. Dissociation Diagram of Wool Drawn (1) As if Acid Amides Were Present (Fig. 9), and (2) As if Amides Were Absent.

metallic cations (Na,K,Ca,Mg,Fe) which are assumed to have been combined with the acid groups of the fiber.* Wool-anion combination curves are sometimes corrected on this assumption.[37] Unsupplemented, the method of ashing cannot show the quantity of organic cations which may be likewise combined, nor the quantity of organic anions which may be combined with the basic groups.

Two things become clear from the above discussion: Though establishing the exact point at which equality of positive and negative charges occur in a given uncontaminated amphoretic body is of real interest, it is perhaps of less practical value than is generally believed, because of the nature and extent of the corrections necessary before the result can be applied to the normal state; secondly, under the circumstances it would seem desirable not to mention an isoelectric point without a description of the specific conditions under which it was obtained, because in all likelihood it is valid only under these conditions.

* Correcting for cationic ash on the assumption that it was bound in carboxyl linkage is not always entirely safe, since an ion like chromium combines with the basic groups when it is present as an anion $(Cr_2O_7^{--})$[37,38].

CALCULATION OF ISOELECTRIC POINTS

Hitchcock[31] has published the following formula for obtaining the isoelectric point of polybasic-polyacidic ampholytes

$$I^2 = K_n K_{n-1} \frac{1 + \frac{2K_{n-2}}{I} + \frac{3K_{n-3}\ K_{n-2}}{I^2} + \dots}{1 + \frac{2I}{K_{n-1}} + \frac{3I^2}{K_{n-1}\ K_{n-2}} + \dots}$$

where I is the hydrogen-ion concentration at the isoelectric point, K represents the dissociation constants (Bronsted system) numbered in order of decreasing magnitude, and n is equal to the highest positive valence of any of the ampholyte ions (numerically equal to the total number of amino groups). This expression can be worked out as follows:

1. *Neutral amino acids.*

$$K_1 = \frac{[^+R^-]\ [H^+]}{[R^+]} \qquad K_2 = \frac{[R^-]\ [H^+]}{[^+R^-]}$$

Calculations

$$[R^+] = \frac{[^+R^-]\ [H^+]}{K_1}$$

$$[R^-] = \frac{[^+R^-]\ K_2}{[H^+]}$$

At the isoelectric point,

$$\Sigma(R^-) = \Sigma(R^+)$$

$$\frac{[^+R^-]\ [H^+]}{K_1} = \frac{[^+R^-]\ K_2}{[H^+]}$$

$$[H^+]^2 = K_1K_2$$

Let $I = [H^+]$ at isoelectric point

then $I^2 = K_1K_2$ (3)

2. *Acid amino acids.*

$$K_1 = \frac{[^+R^-]\ [H^+]}{[R^+]} \quad K_2 = \frac{[^-\dot{R}^-]\ [H^+]}{[^+R^-]} \quad K_3 = \frac{[^-R^-]\ [H^+]}{[^-\dot{R}^-]}$$

Calculations:

$$[R^+] = \frac{[^+R^-]\ [H^+]}{K_1}$$

$$[R^-] = \frac{K_2\ [^+R^-]}{[H^+]}$$

$$[\dot{R}^-] = \frac{K_3\ [^-\dot{R}^-]}{[H^+]} = \frac{K_3\left(K_2\frac{[^+R^-]}{[H^+]}\right)}{[H^+]}$$

at I, $\Sigma(R^-) = \Sigma[(R^-) + 2(\dot{R}^-)]$

$$\frac{[R^-]\ [H^+]}{K_1} = \frac{K_2\ [^+R^-]}{[H^+]} + \frac{2K_2K_3[^+R^-]}{[H^+]^2}$$

$$[H^+] = K_1K_2 + \frac{2K_1K_2K_3}{[H^+]}$$

$$I^2 = K_1K_2\left(1 + \frac{2K_3}{I}\right) \qquad (4)$$

3. *Basic amino acids.*

$$K_1 = \frac{[^+\dot{R}^+]\ [H^+]}{[^+R^+]} \quad K_2 = \frac{[^+R^-]\ [H^+]}{[^+\dot{R}^+]} \quad K_3 = \frac{[R^-]\ [H^+]}{[^+R^-]}$$

Calculations:

$$[R^+] = \frac{[^+R^-]\ [H^+]}{K_2}$$

$$[^+\dot{R}^+] = \frac{[^+\dot{R}^+]\ [H^+]}{K_1} = \frac{\frac{[^+R^-]\ [H^+]^2}{K_2}}{K_1}$$

$$[R^-] = \frac{[^+R^-]\ K_3}{[H^+]}$$

at I, $\Sigma[2(^+R^+) + (R^+)] = \Sigma(R^-)$

$$2\frac{[^+R^-]\ [H^+]^2}{K_1K_2} + \frac{[^+R^-]\ [H^+]}{K_2} = \frac{[^+R^-]\ K_3}{[H^+]}$$

$$[H^+]^2 = \frac{K_1K_2K_3}{2[H^+]K_1}$$

$$I^2 = K_2K_3\left(\frac{1}{1 + \frac{2I}{K_3}}\right) \qquad (5)$$

4. *6 Groups (3 amino, 3 carboxyl).*

$$K_1 = \frac{[^+R^+]\ [H^+]}{[^+\dot{R}^+]} \quad K_2 = \frac{[R^+]\ [H^+]}{[^+R^+]} \quad K_3 = \frac{[R]\ [H^+]}{[R^+]}$$

$$K_4 = \frac{[R^-]\ [H^+]}{[R]} \quad K_5 = \frac{[^-R^-]\ [H^+]}{[R^-]} \quad K_6 = \frac{[^-\dot{R}^-]\ [H^+]}{[^-R^-]}$$

Calculations:

$$[R^+] = \frac{[R]\ [H^+]}{K_3}$$

$$[^+R^+] = \frac{[R^+]\ [H^+]}{K_2} = \frac{\frac{[R]\ [H^+]^2}{K_3}}{K_2}$$

$$[^+\dot{R}^+] = \frac{[^+R^+]\ [H^+]}{K_1} = \frac{\frac{[R]\ [H^+]}{K_2K_3}}{K_1}$$

$$[R^-] = \frac{K_4[R]}{[H^+]}$$

$$[^-R^-] = \frac{K_5\ [R^-]}{[H^+]} = \frac{K_5\left(\frac{K_4\ [R]}{[H^+]}\right)}{[H^+]}$$

$$[^-\dot{R}^-] = \frac{K_6\ [^-R^-]}{[H^+]} = \frac{K_5K_6\left(\frac{K_4\ [R]}{[H^+]}\right)}{[H^+]}$$

At I, $\Sigma[3(^+\dot{R}^+) + 2(^+R^+) + (R^+)] = \Sigma[(R^-) + 2(^-R^-) + 3(^-\dot{R}^-)]$

$$3\frac{[R]\ [H^+]^3}{K_1K_2K_3} + 2\frac{[R]\ [H^+]^2}{K_2K_3} + \frac{[R]\ [H^+]}{K_3} = \frac{K_4[R]}{[H^+]} + 2\frac{K_4K_5[R]}{[H^+]^2} + 3\frac{K_4K_5K_6[R]}{[H^+]^3}$$

$$I^2 = K_3K_1\frac{1 + \frac{2K_5}{I} + \frac{3K_5K_6}{I^2}}{1 + \frac{2I}{K_2} + \frac{3I^2}{K_1K_2}} \qquad (6)$$

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APPLICATION TO WOOL DISSOCIATION

This method can be extended to apply to all dissociating groups in wool. Using the dissociation constants illustrated in Fig. 8, and the numbers representing group frequencies (Table 1), the calculated isoelectric point for the curves of Figure 9 is at pH 9.8; for the curves of Figure 10, pH 8.7; and for those of Figure 11, pH 4.2 and 9.8.

CONCLUSION

The purpose of this report has been to attempt to establish as well as possible a basis for better understanding of the combination of wool with acid, base, and salt. The many weaknesses indicate clearly enough how tentative and subject to modification the whole scheme is, but it seems to be the soundest approach toward eventual solution of the problem.

Reports which may follow on experimental work will show where agreement and disagreement lies. In order to ease the mind about several critical points, and give all possible assurance* that the ideas being presented were valid, much data had to be collected in conjunction with the present paper on theory, and are at hand; but much work remains.

* It is not easy to accept even tentatively many conclusions which cannot be substantiated repeatedly by actual experiment. Many such confirming experiments could not be run, and the report is considerably weakened by this failure. It may be possible to remedy the situation later.

ACKNOWLEDGEMENT

The writer is indebted to Wilbert Carr, Jr. for much help in the mathematical treatment of this subject, and to Dr. William T. Bovie for reading the paper, and making a number of helpful suggestions.

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TRADE NOTES • NEW PRODUCTS

OBITUARY

LEO ALTENBERG, department sales manager of the Calco Chemical Division, American Cyanamid Company, died in Beth Israel Hospital, New York, on Thursday, September 13, 1945. He had been confined to his home at 171 Beach 138 St., Belle Harbor, Long Island, for several months, due to failing health.

Leo Altenberg

Mr. Altenberg, a chemical engineer, was graduated from Columbia University in 1915. In 1922 he founded the Gaskill Chemical Corporation in Brooklyn, New York, manufacturers of fur dyes, of which he was president.

The plant, which subsequently moved to Newark, N. J., was acquired by Calco in September, 1929. He remained with Calco in charge of fur dye sales.

Mr. Altenberg is survived by his widow and three sons.

• JOIN MILTON HARRIS

Dr. William E. C. Yelland and Dr. Samuel W. Waisbrot have joined the staff of the Milton Harris Associates, Washington, D. C. Before coming to Washington, Dr. Yelland was Section Leader of the Colloids and Fibers Group in the Research Department of the Corn Products Refining Company, Argo, Illinois. He also has worked in the Rayon Laboratory of the same company at Edgewater, New Jersey, and was for several years on the staff of the Massachusetts Institute of Technology as a Fellow of the Textile Research Institute.

Dr. Waisbrot came to Washington from the Organic Division of the Celanese Corporation of America, Newark, New Jersey, and prior to that he was located for several years at the Western Regional Research Laboratory, Albany, California.

• COURSE ON COLOR

For the third successive year the Board of Education of New York City is giving a course on "Color, Color Systems and Coloring Agents" at the Textile Evening High School, 18th Street near 9th Avenue, New York. The class meets on Thursday evenings from 7:00 p.m. to 9:00 p.m. and will run for about 20 sessions. The instructor is William H. Peacock, Assistant Color Laboratory Manager, Calco Chemical Division, American Cyanamid Company, who has had many years of experience with coloring problems on all types of materials.

The class will study the functional and psychological uses of color in selling, industry, interior decoration, personal attire, and design; the Munsell, Ostwald, and other systems of color order; the classification of coloring materials; color matching, color harmony, the use of spectrophotometric data, and the thirty or more factors that influence the judging of color effects. Applicants need not be residents of New York but preferably should be high school or college graduates. The first session was held Thursday, September 27, 1945. Applicants may register evenings at the school.

• ANNUAL MEETING, C.T.I.

The Cotton-Textile Institute will hold its 19th annual meeting at the Waldorf-Astoria Hotel, New York City, on October 24 and 25.

The meeting will consist of two general sessions and five forums at which problems confronting the industry will be analyzed and discussed by specialists.

• JOINS INTERCHEMICAL EXPORT DIVISION

Interchemical Corporation has engaged Anthony Garcia for liaison work in Latin America, according to C. A. Richards, Director of the Export Division. Mr. Garcia was born in Buenos Aires, has spent many years in France, and is also well acquainted with the United States. He speaks English, Spanish, Portuguese, French and German.

Anthony Garcia

For the past five years Mr. Garcia was associated with Sherwin Williams. He has a background of experience in dry colors, inks, varnishes and textile colors.

After a thorough study of Interchemical products Mr. Garcia will leave for Argentina and Brazil to make surveys of market possibilities, consult with Interchemical representatives and assist them in increasing their outlets.

• NUODEX BULLETIN

The availability of a new bulletin, "The Quantitative and Qualitative Determination of Copper, Zinc, and Mercury in Treated Fibers and Fabrics" has just been announced by Arthur Minich, Vice-President in charge of Research and Development, Nuodex Products Co., Inc.

Compounds of copper, zinc, and mercury are commonly used as fungicides to rotproof thread, yarns, twine and rope. This bulletin, it is believed, presents for the first time simple but detailed methods by which the textile or cordage manufacturer can analyze treated materials to control the fungicide content.

The analyses described have been selected by the Nuodex Laboratories to combine maximum accuracy, speed, convenience of use under practical working conditions, and applicability to treated fabrics or cordage from which the metal must be extracted before the analysis can be completed.

Anyone interested in securing a copy of this bulletin may obtain it free of charge by writing Nuodex Products Co., Inc., Elizabeth, F, New Jersey.

• JOINS ALROSE CHEMICAL

Alrose Chemical Company of Providence, R. I. announces that Alfred N. Henschel has joined its technical staff. Mr. Henschel has been in the textile printing and finishing industry since 1930 and has worked both in the North and the South. Mr. Henschel will be associated with Archie Stevenson in the technical service offered by the company in rendering assistance on the newly developed fabric stabilization processes for wool, rayon and cotton worked out by Alrose Chemical Company.

• JOINS AMERICAN CYANAMID

The American Cyanamid Company has announced the appointment of George C. Ramey as advertising manager and director of promotion and publicity of its Textile Resin Department.

Mr. Ramey was recently released from active duty as a lieutenant in United States Naval Aviation.

George C. Ramey

Just prior to entering the Navy, Mr. Ramey was connected with Clarence Whitman and Sons as sales manager of the Wilkes Barre Lace Manufacturing Company. He also served as sales manager of the piece goods, hosiery and knitwear departments and later as promotional sales supervisor of Marshall Field and Company, Manufacturing Division.

For a number of years Mr. Ramey was associated with the Forstmann Woolen Company in the capacity of salesman to many of the company's leading coat and suit manufacturing accounts.

The Textile Resin Department of American Cyanamid Company is now engaged in the marketing of a new line of melamine resin and other synthetic resin finishes with applications in every textile field.

• JOINS AMERICAN VISCOSE

Frank F. Hilson, formerly with Good Housekeeping Magazine and H. K. McCann Co., has joined the advertising department of the American Viscose Corporation. He will handle sales promotion and merchandising work in connection with the company's "Crown" Tested Plan under which fabrics containing the company's rayon are tested for service qualities.

• NEW C & C CHEMICALS

The 12th edition of the catalog "Synthetic Organic Chemicals," has just been published by Carbide and Carbon Chemicals Corporation, a Unit of Union Carbide and Carbon Corporation. "Synthetic Organic Chemicals" presents in condensed form, up-to-date information on the properties, uses, and specifications of more than 160 products sold by this Corporation. This edition includes data on 34 products not included in previous editions and contains new chapters on acetals, sulfur compounds, polyethylene glycols, hydroxyethyl cellulose, and plasticizers—making this book more than ever an important reference manual of industrial aliphatic chemistry. Revised tables also contain shipping information and specifications of particular value to purchasing agents. Copies of the 12th edition of "Synthetic Organic Chemicals" (F-4372) may be obtained by writing to Carbide and Carbon Chemicals Corporation, 30 East 42nd Street, New York, 17, N. Y.

• NEW MATHIESON PLANT

A new plant which will double the output of sodium chlorite is now being added to the Niagara Falls, New York, production facilities of The Mathieson Alkali Works, according to George W. Dolan, president of the company. Construction cost of the new building is estimated at $35,000 and its total cost at about $323,000.

Sodium chlorite was made commercially available by Mathieson in 1940. Since then, its major uses have been as a bleach and oxidant in the textile and paper pulp industries. During the past year, it has come into use for the removal of tastes and odors in a new process for treating public water supplies, but only a few cities have been able to take advantage of this development, Mr. Dolan stated, because of the inadequate supply of the chemical.

The new plant is badly needed, Mr. Dolan said, as present production capacity is far below the demand for sodium chlorite. It is expected that many promising applications will be developed when increased production makes it possible to take care of present markets and supply enough of the chemical for plant scale experimentation.

• ELECTED PRESIDENT, MONSANTO

William McNear Rand recently was elected president of Monsanto Chemical

Company, succeeding Charles Belknap, who will continue with the company as chairman of its executive committee. Mr. Rand, now a vice president, will assume his new office October 1.

In announcing Mr. Rand's election, Board Chairman Edgar M. Queeny said that Mr. Belknap agreed to extend his service beyond the normal retirement date as executive committee chairman and board member at the request of the board of directors.

For the last eight years, Mr. Rand has been a Monsanto vice president and since November, 1943, when he became a member of the executive committee, has had his headquarters in St. Louis.

• KEARNY PERSONNEL CHANGES

Kearny Manufacturing Company, Inc., Kearny, N. J. and its subsidiaries and affiliated corporations announce that C. F. Dulkin, President of the organization since April 1928, has tendered his resignation, effective August 31, 1945.

Walter P. Rutley of Montclair, N. J., Sales Manager of the organization for the last six years, has been elected President, effective September 1, 1945.

Mr. Dulkin will continue to serve the company as a Director and in an advisory capacity. Geo. Westwater of Irvington, N. J. and W. O. Slimback of Kearny, N. J. will continue on the staff as Vice Presidents, and Robert H. Sommer of Kearny, N. J. as Secretary-Treasurer.

• ONYX INTERNATIONAL

The name of Onyx Chemical Corp., Warren and Morris Sts., Jersey City, N. J., has been changed to Onyx International. It is stated that the new name more completely designates the activities of the company. The corporate structure of the company is in no other way affected.

Keep on Buying and HOLDING Bonds!

• CONCENTRATION OF CELANESE ACTIVITIES

The initial step in the concentration of the technological and research activities of Celanese Corporation of America in the fields of textiles, plastics and chemicals in a single central laboratory was undertaken with the announcement that the company has acquired buildings for that purpose in Summit, New Jersey, twelve miles outside of Newark.

The buildings were occupied by the Edison Junior High School. The company intends to convert the school into a modern industrial laboratory and, later, make extensions which will double the present size of the buildings.

Work on the project is expected to get under way shortly, and it is estimated that eventually approximately 500 scientists, chemists and skilled technicians will be at work in the new unit.

The Celanese laboratory will consolidate the corporation's experimental and research work which is now carried on at various plants throughout the country.

• CLASSIFIED ADVERTISEMENTS •

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $6.25 per column inch or less per insertion.

POSITION WANTED: Woolen Cloth, Wet and Dry Finishing Foreman. Several years experience. Box 740.

WANTED TECHNICAL SALES ASSISTANT: Rare opportunity to become permanently connected with nationally recognized manufacturer of textile processing specialties. Prefer graduate of textile institute with mill experience. Will act as assistant to District Manager covering Pennsylvania, Maryland, Delaware, Virginia. Salary plus bonus. Write giving complete educational and business background. Replies held in strict confidence. Our organization knows of this advertisement. Box 748.

WANTED: Textile chemist and colorist, technical education, practical experience in supervising dyeing and finishing. Write giving age, education, experience and salary requirements. Box 749.

WANTED: Plant Chemist with experience in processing rayon, acetate and cotton piece goods to work between Lab and plant, developing new methods of dyeing and finishing. Give full details of practical experience. Box 751.

POSITION WANTED: Graduate textile chemist fourteen years overseer of dyeing and bleaching knit-goods. Desires position with dyestuff or chemical concern as salesman and demonstrator. Box 754.

POSITION WANTED: Married man 37 years old with 17 years bleaching, dyeing and finishing cotton and rayon piece goods experience, 5 years as plant supervisor in small finishing mill, at present overseer of dyeing in large mill desires a change. Box 755.

WANTED: Textile chemist for research work—both laboratory and field work. Permanent position. Excellent opportunities. Write for application. Location Upstate New York. Box 756.

WANTED: Assistant Dyer by National Hosiery Mills, Inc., Indianapolis, Indiana. Preferably man 25 to 35 years of age. Man with experience in Chemistry and Dyeing preferred. Contact J. A. Goodman, President.

WANTED: First-Class Colorist for Screen Printing Plant. Box 757.

WANTED: Salesman to take over Southern territory by an old and well established dyestuff concern, manufacturing dyestuffs and textile specialities. State experience and qualifications. Box 758.

WANTED: Textile chemist with practical experience with Rayon, Acetate and Mixtures. State previous experience and salary desired. Box 759.

WANTED: Textile colorist for work in Standardization Laboratory of dye manufacturer, also involves work on application of dyestuffs. Our employees have been notified. Send snapshot, statement of training and experience. Box 760.